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Research Highlights Old, New Fields for Development

In the ongoing search for new natural gas technologies, projects run the gamut from understanding hydrocarbon migration to getting the most out of the least productive wells.

This issue of *GasTIPS* contains a veritable smorgasbord of research initiatives aimed at developing technology to find and develop domestic gas reserves. No one technology holds all the answers, and these projects represent the work of thousands of bright minds attacking the problem from every conceivable angle.

On the exploration side, an article from Cornell University describes a study that has discovered and documented the effects gas can have on oil through a process called gas washing. Modeling of variations in n-alkane presence from the north end of the Gulf of Mexico study area to the south end indicates this variation is expected from the changing pattern of sediment deposition. The study indicates the chemistry of the gas and washed oils carry information on the current pattern of subsurface petroleum migration relevant to exploration for subsurface hydrocarbon resources.

In drilling news, a new product called IntelliPipe®, developed jointly between the U.S. Department of Energy (DOE), NOVATEK and Grant Prideco, promises to replace mud-pulse telemetry in providing high-speed information from downhole during the drilling process. The availability of this real-time data allows for bi-directional feedback and control for downhole steering assemblies to more accurately locate and place the well in a targeted reservoir. Also, the efficiency of drilling operations can be optimized, costs reduced and safety improved. The technology potentially



Stripper wells are getting attention as a host of new technologies attempt to squeeze out the remaining reserves.

enables the improvement and increase of underbalanced drilling technology, which can be used to increase drilling speed and decrease formation damage.

Many of the projects discussed deal with production issues. A key concern in the United States is the vast number of stripper wells. A stripper well is defined as a well that produces less than 10 b/d of oil or less than 60 Mcf/d of gas. These wells are important to the energy security of the United States, as they represent 15% of the oil and 7% of the gas produced. Therefore, continued production from these wells is increasingly dependent on new technologies, which will keep them economical.

Recognizing that most stripper wells are operated by smaller independent operators who have neither the funds nor the staff to develop new technologies, the DOE through the National Energy Technology Laboratory developed and sponsors the Stripper Well Consortium (SWC). The SWC offers

operators across the United States a forum to discuss with technology developers the operating problems they face in their daily operations. The SWC recently held its third annual meeting and accepted 13 proposals for full or partial funding, which also are discussed in this issue.

Other articles deal with hydrate inhibition, the treatment of sour gas and the potential for using salt caverns to store liquefied natural gas from offshore installations. We hope you'll find this issue of *GasTIPS* informative. Please contact the individuals listed at the end of each article to obtain more information on specific topics. If you have any questions or comments, please contact managing editor Rhonda Duey at rduey@chemweek.com. ♦

The Editors

Very High-Speed Drill String Communications Network: An Enabling Technology

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A new technology solves drillstring-coupling problems, making downhole data transmission a reality.

The quest for high-speed data transmission has been a Holy Grail in the exploration and drilling disciplines since the inception of the ability to evaluate the downhole-drilling environment and accurately characterize the formation being drilled while precisely navigating wellbores to targeted reservoirs in real time. Since 1939, technology has been proposed to provide data from downhole to the surface. The technical barrier has been the couplings between the discrete pipe sections comprising the drillstring.

For more than 60 years, the oil and gas industry has struggled with the problem of a drill pipe connection, or “tool joint,” that would stand up to the wear and tear of hostile drilling conditions and operations, yet provide a reliable and rapid data transmission connection. Largely because of this stumbling block, developers turned to a technology called “mud pulse telemetry” in the mid-1970s.

Mud pulse telemetry eliminates the need to hard-wire pipe and electrical connections and transmits data as pressure pulses through fluid circulated to clean the cuttings out of the wellbore. But the excruciatingly slow pace of mud pulse telemetry – 3 to 10 bits per second – often means data resolution and tool reliability is so poor the driller cannot make crucial decisions in real time. Often, time-consuming operations are required to retrieve the downhole data, or drilling has to stop while other procedures are employed to confirm the low-resolution data pulsed to the surface. Additionally, underbalanced drilling (UBD) operations utilizing foams and gases cannot be used with the current mud-pulsed system.

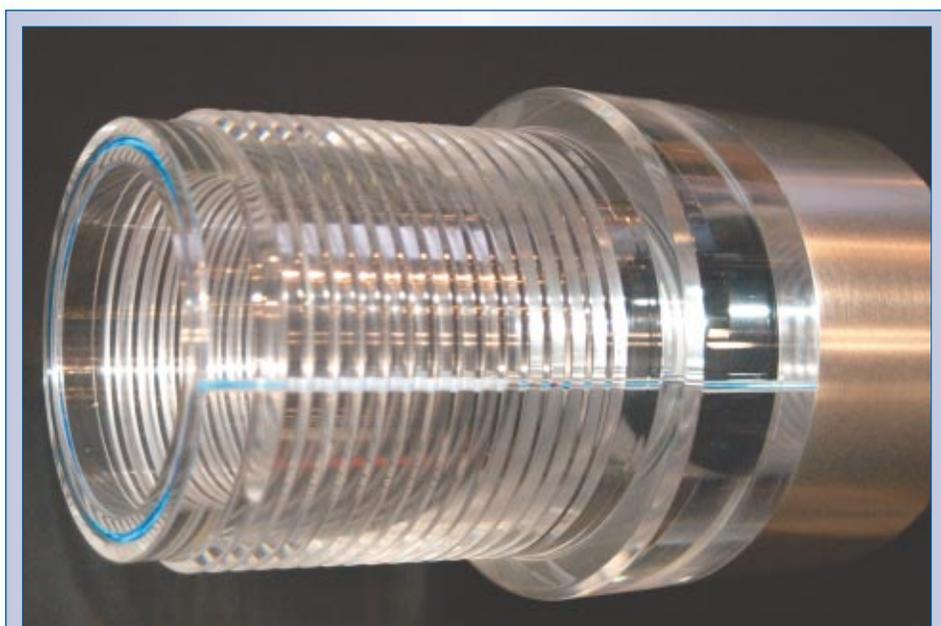


Figure 1: The above coupler permits data to be sent across the connection and through a high-speed cable attached to the inner-pipe wall.

Downhole Internet: The Solution

In 1997 NOVATEK in Provo, Utah, was funded by the U.S. Department of Energy’s National Energy Technology Laboratory (NETL) to develop a steerable Mud Hammer System. As part of that research, a high-speed data transmission system was needed. NOVATEK addressed that need and found a large technology gap existed and would require substantially more resources than a supporting project task would allow. Additionally, in accomplishing the research, a better mode of data transmission was identified. Grant Prideco, the world’s largest drill pipe manufacturer, began working with NOVATEK on the

data system in early 2000 and formed a new corporation called IntelliServ® to commercialize the system. In 2001, NETL partially funded the spin-off technology development of a high-speed downhole communications (telemetry) system now referred to as IntelliPipe®.

The key to the new system is a unique non-contacting coupler embedded in connections between 30-ft sections of drill pipe (Figure 1). The concept allows the IntelliPipe to be used like regular drill pipe without any special handling of the pipe by the rig hands.

The concept is to passively link discrete components together into a downhole communication network. Identified as IntelliCom™, this link is comprised of a ring-shaped transducer that transmits

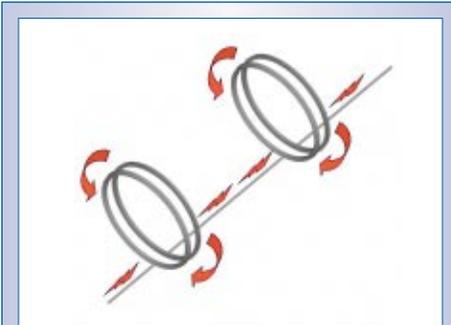


Figure 2: The non-contact feature of IntelliCom's ring-shaped transducer link allows it to be embedded and protected within drillstring components.

data to another component without direct electrical contact (Figure 2). This makes the system much more reliable and robust than other hardwired telemetry concepts tried in the past and orders of magnitude faster than the current mud pulse system.

The unique geometry design of Grant Prideco's line of eXtreme Torque® (XT) drill pipe provides an ideal location for the IntelliCom components (Figure 3). An armored data cable running the length of the drill pipe completes the data path between the IntelliCom links or mated tool joints (Figure 4).

IntelliPipe is the basic building block of a modular downhole data transmission line. Once the transmission line is in place, information may move between various members of the drilling assembly, much like information can be shared by several users on a network or Internet. The components comprising this "Internet" can be at the surface, at the bit or anywhere along the drillstring. Just like the Internet, addressable nodes can be defined along the drillstring. These nodes can be individual tool joints or control devices including jars, motors, bits, measurement-, logging- or seismic-while-drilling (MWD, LWD and SWD) sensors as well as other downhole tools (Figure 5). At each node identifiable events can be correlated to a particular region of the well.

Proprietary software and hardware

controls the flow of information. A key device called the IntelliLink™ controls the flow of information and boosts the data signal strength (Figure 6). This important component is housed in a modified full-length joint of drill pipe and includes a large through-bore to allow for low fluid friction pressure losses and through-access.

The technology is applicable to all types of threaded drillstring assemblies, including reamers, jars, stabilizers and other subs. Rotating joints, such as swivels and downhole motors, do not impair the use of the IntelliCom technology. A data swivel sub at the top of the drillstring allows the transmitted signal to be redirected into a drillstem data server and distributed even to the World Wide Web after encryption for access by company personnel.

Enabling Technology and Benefits of the IntelliServ Network

The real-time characterization of a reservoir during the drilling process is one of the premier applications of the IntelliServ network. These include LWD, MWD and SWD. The availability of this real-time data allows for bi-directional feedback and control for downhole steering assemblies to more accurately locate and place the well in a targeted reservoir (Figure 7).

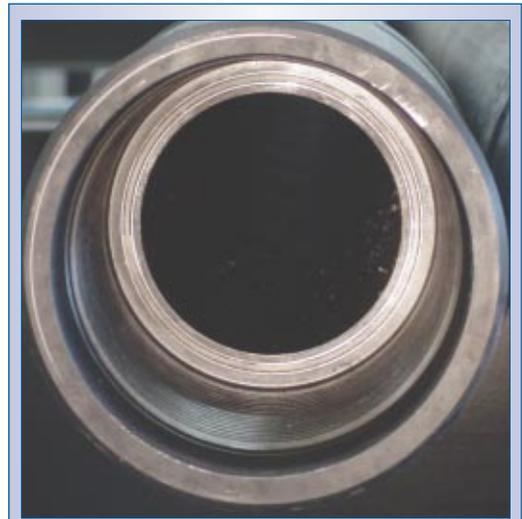


Figure 3: Mated segments of these double-shouldered drill pipes provide the connectivity for the high-speed data network of IntelliPipe.

Increased efficiency, cost reduction and improved safety is possible since the network allows for more precisely locating stuck pipe, monitoring drillstring and bit vibration, actual downhole rotation speed, weight on bit, monitoring pressures up and down the well for kick detection, and seismic look-ahead data transmitted over the network.

The IntelliServ network potentially enables the improvement and increase of UBD technology, which can be used to increase drilling speed and decrease formation damage. The network is not affected by the type of fluid used to drill a well, unlike current MWD, LWD and SWD telemetry systems. Therefore,

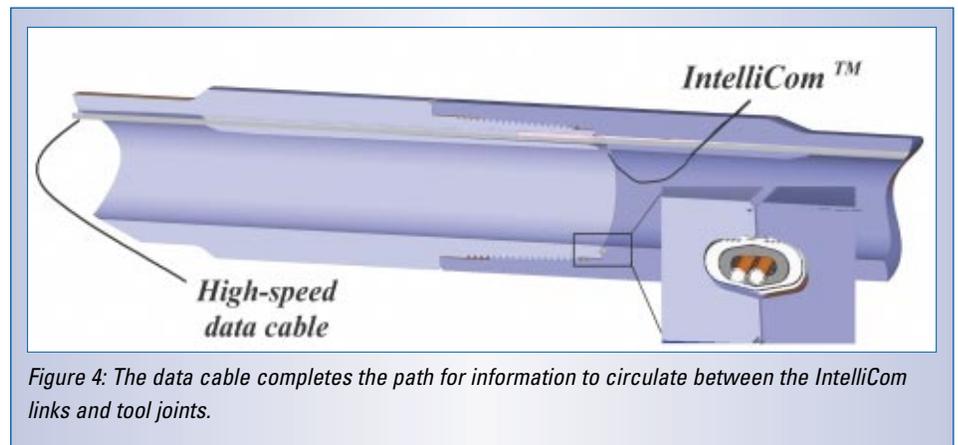


Figure 4: The data cable completes the path for information to circulate between the IntelliCom links and tool joints.

better productivity in under-pressured and/or fluid sensitive reservoirs using UBD is possible.

Status of the Technology

Initial tests of the prototype were conducted in a 1,000-ft well at IntelliServ's test facility in Provo and at a 2,000-ft well at the Gas Technology Institute's Catoosa test site in Oklahoma. Full-scale tests have included multiple makeups (50 to 150) to full torque on several joint pairs. Data transmission rates are approaching 2 million bits/sec.

Additionally, actual drilling tests have been concluded at the U.S. Department of Energy's Rocky Mountain Testing Center near Casper, Wyo. A 6,000-ft already-drilled well was chosen for this test. A drillstring comprising 121 joints of IntelliPipe, IntelliLinks and Intelli-Heavyweight™ (3,827ft) was successfully run in the well and able to establish communication along the entire string

for the duration of the testing. A data rate of 2 megabit/sec was established through the system for all tests. Total string length, including the bottomhole assembly, was 4,531ft. In this string, five IntelliLinks were used as network nodes and data collection sites.

Full-scale tests have been supplemented by bench-top laboratory testing. For example, seals used in cable connections have been tested in a pressure vessel at simulated borehole conditions of 391°F and 25,000psi. Such testing continues in an effort to further improve the transmission range and drilling robustness of the system.

The process of inserting a wire permanently inside a joint of drill pipe requires certain modifications to be made to the pipe. These modifications have been analyzed by Grant Prideco engineers using predictive FEA and laboratory testing and have shown the pipe strength and integrity of the pipe is unchanged.

Further Developments

Currently, this project is entering the third and final phase of activity, which is to get a complete drilling string into the field, establish high-speed communications with third-party down-hole tools and prepare the system for commercial introduction.

Development efforts are underway to improve the flexibility and capabilities of the IntelliServ drilling network software and hardware. A key area of focus is integration of existing downhole measurement and logging devices with the IntelliPipe hardware and network system. Cooperative efforts with major tool manufacturers are underway. Other new tools and applications for the network also are being developed.

A second key area of present focus is improving the passive transmission range of the system. As mentioned above, the present system has demonstrated transmission

of 1,000ft prior to needing a boost in signal level. Improvements to transmission line efficiency and electronic module sensitivity are expected to bring as much as a five-fold increase in this passive range. Work to bring about these improvements already has begun.

A third area of focus is to extend the transmission line to other drillstring elements including jars, drill collars and miscellaneous subs. Work in each of these areas is progressing. As a matter of particular interest, IntelliServ is working closely with a major manufacturer of drilling jars, and a design for a wired jar is expected to be tested soon.

Finally, further work is needed to increase the high-pressure and high-temperature capabilities of the IntelliCom components and the network electronics so these may be used in the deepest wells and under the most severe drilling conditions.



Figure 5: IntelliPipe is the basic building block of a modular downhole data transmission line.

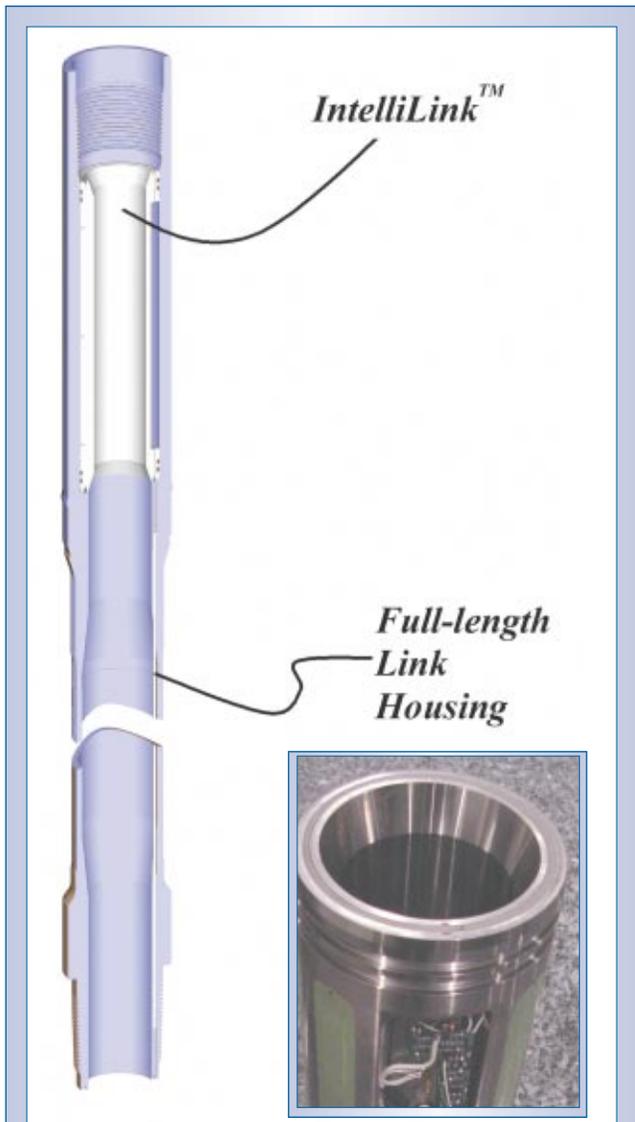


Figure 6: The software and hardware inside the IntelliLink (inset) help control the flow of information.

Introduction and Commercialization to the Petroleum Industry

Official introduction of this technology to the petroleum industry occurred at the

fairly benign to normal drilling operations, since the test will largely consist of handling drill pipe. System failures encountered in the testing, if any, are expected to have minimal impact on the drilling process

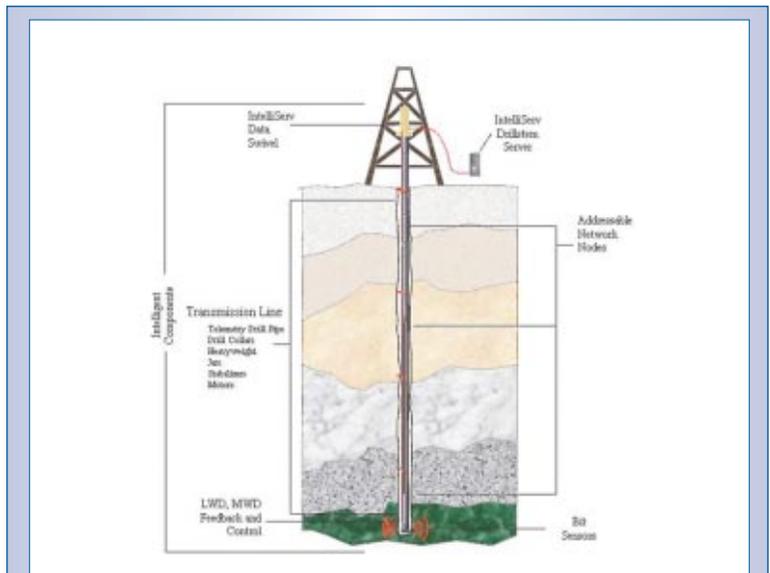


Figure 7: With the IntelliServ network, the efficiency of drilling operations can be optimized, costs reduced and safety improved.

2002 Society of Petroleum Engineers Annual Conference. Initial commercial application of the IntelliServ system is anticipated during the fourth quarter of 2003.

A major effort and key to all this work is field qualification of the system. IntelliServ is seeking opportunities to field-test the data transmission system in low-risk applications. Such testing, though not without risk, is seen to be

and can be corrected during normal tripping of the string. Field testing of the system is expected to continue throughout 2003.

Conclusions

IntelliServ is one of the most enabling technologies to be developed recently for the petroleum industry. The impact is far reaching. The technological advancement expected in the overall drilling process will result in faster well drilling, thereby reducing well costs. The “smart pipe” itself is the building block of a downhole “Internet system” that will allow for the first time high-speed bi-directional communication with various tools, and allow economic reservoir characterization and precise navigating of a well while drilling in real time.

For more information, please contact John Rogers at jrogers@netl.doe.gov, (304) 285-4880. ♦



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Security, Economy and Capacity—A Salt Cavern-Based LNG Receiving Terminal

By Michael M. McCall,
Conversion Gas
Imports, LLC

New research indicates salt caverns could provide a cost-effective storage method for liquefied natural gas.

Salt caverns provide an integral link in the logistical requirements of the natural gas, natural gas liquids, petrochemical and refining industries in the United States. The purpose of this paper is to present preliminary results of seminal research involving the use of salt caverns in the receipt of seaborne liquefied natural gas (LNG). The research is conducted under cooperative agreement with the U.S. Department of Energy's (DOE) National Energy Technology Laboratory (NETL).

Cooperative Agreement:

DE-FC26-02NT41653

Project Title: Examine and Evaluate a

Process to Use Salt Caverns to Receive Ship-Borne Liquefied Natural Gas (LNG)

Introduction

The DOE cooperative research project on which this paper is based indicates that salt cavern-based receiving terminals in onshore and offshore locations on the Gulf Coast could be built at reduced capital cost and have less than half the operating costs, significantly higher delivery capacity, shorter construction time and be much more secure than conventional liquid tank-based terminals. The research describes an onshore LNG-receiving facility in southwest Louisiana (Figure 1) and an LNG-receiving facility built 50 miles offshore in Vermilion Block 179. The considerable natural gas infrastructure in this area in offshore gathering, and onshore intrastate and interstate pipelines has considerable capacity available to help meet increasing gas demands in the United States. There is a significant body of knowledge and practice concerning natural gas storage in salt caverns, and there is a considerable body of knowledge and practice in handling LNG, but there has never been any attempt to develop a process whereby the two technologies can be combined. Salt cavern storage is infinitely more secure than surface storage tanks, far less susceptible to accidents or terrorist acts and much more acceptable to the community. Salt cavern natural gas storage is known for its very high deliverability that is instantaneously available to meet

variable demands in the gas grid. The addition of LNG receiving to cavern storage would allow the storage facilities to be replenished during periods of continued high demand or to replace declining gas production.

LNG imports are expected to become an increasingly important part of the U.S. energy supply, and the capacities to receive LNG securely, safely and economically must be expanded. This research confirms the feasibility of salt cavern LNG-receiving terminals onshore and offshore. Such terminals can be quickly built and provide additional import capacity into the United States, exceeding 10 Bcf/d in the aggregate.

The performance of work under this agreement is based on U.S. Patent 5,511,905 along with pending U.S. and foreign patent applications. The cost-sharing participants in the research are the NETL, BP America Production Co., Bluewater Offshore Production Systems (USA) Inc. and HNG Storage LP.

Conventional Tank-Based LNG Receiving Facility

A typical tank-based facility will have insulated tank storage capacity for cargo from two to three ships or about 5 Bcf to 8 Bcf at standard conditions (250,000 cu m to 380,000 cu m in liquid form). The terminal will always have an LNG inventory in its storage tanks to keep everything cooled down. Typically, the high-pressure pumps and vaporizers are the units' limiting send-out as the facility can receive a cargo in 24 hours but takes from 3 days to 6 days to discharge that volume as gas to the pipelines. There are four LNG terminals in the United States of this design, one of which is being refurbished.

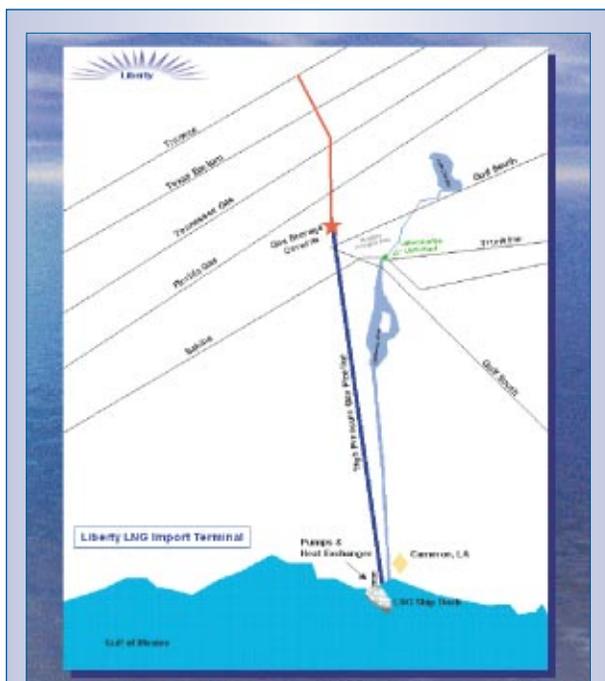


Figure 1: The Liberty LNG Terminal would connect to seven major natural gas pipelines having a takeaway capacity of 3 Bcf/d.

All have announced expansion plans, but collectively the expanded terminals fall far short of the projected imports of LNG by 2020. Various alternate designs using cryogenic tank storage on floating vessels, shipboard regasification units or gravity-based structures generally take this same model and move it to sea.

LNG cryogenic storage tanks are expensive to build and maintain. Several cargoes scheduled to be received after Sept. 11, 2001, have been delayed because of security concerns. There is therefore a need for a more secure, more economical and higher-capacity way to receive, store and distribute LNG imports than has been done in the past.

Salt Cavern-Based LNG-Receiving Facility

The application of conventional salt cavern storage technology, augmented by new technology in the area of pumps, heat exchangers and facility design, could marry LNG and salt caverns into a highly secure, economical and flexible method to expand the importing nation's energy supply. In the Liberty LNG Terminal, the ship unloading occurs 35 miles from the cavern storage site. In a conventional terminal, the liquid storage tanks must be in close proximity to the ship discharge site, and considerable inventory is maintained between ships' calls (Figure 2).

There are a number of salt formations, offshore and near shore, or navigable waters where caverns could be solution-mined and developed into LNG-receiving terminals. Salt cavern gas storage facilities have very high deliverability instantaneously available to the pipeline system, far higher than LNG vaporization capacities in conventional LNG terminals.

Critical Elements

The major critical elements revealed in the research are:

- a method to moor and offload an LNG ship
- LNG pumps sufficient to create cavern injection pressures and volume

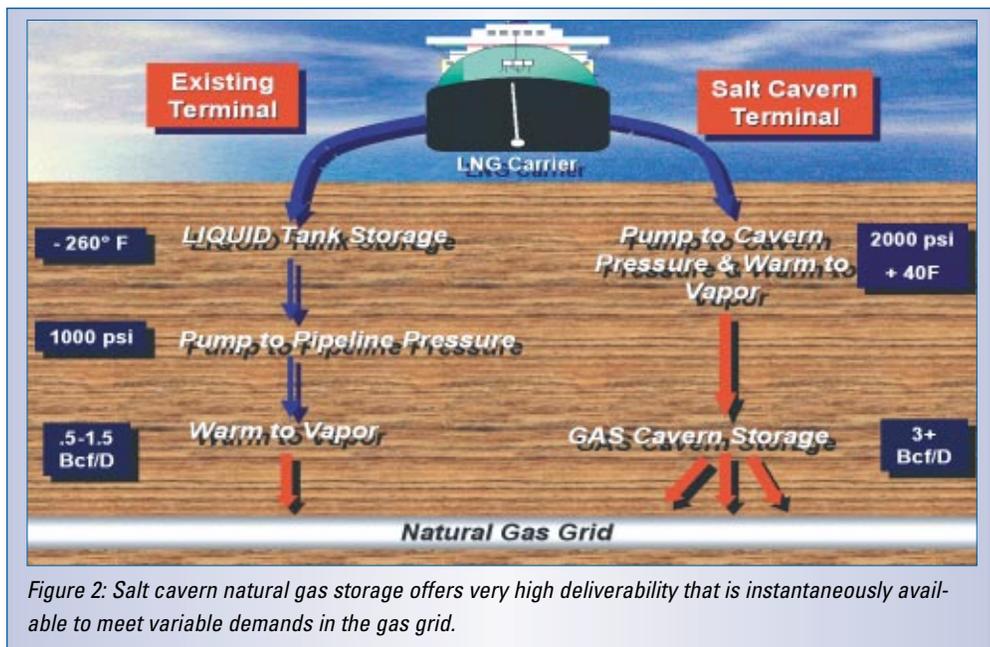


Figure 2: Salt cavern natural gas storage offers very high deliverability that is instantaneously available to meet variable demands in the gas grid.

capability to allow acceptable ship discharge times

- a heat exchanger design that will economically warm the LNG at high pressure and high volumes
- navigable waters sufficient for an LNG carrier to approach
- salt formations suitable for cavern development
- a pipeline infrastructure sufficient to carry large volumes of gas to market.

Mooring and Offloading

A conventional International Society of Gas Tanker and Terminal Operators jetty and mooring configuration alongside a navigable waterway was chosen to fit the requirements of the onshore Liberty LNG site. For the offshore application, the research describes a new design developed by Bluewater Offshore Production Systems (USA) Inc. for the offshore mooring and LNG transfer system, the regasification and the storage of the gas in offshore salt caverns. The system is developed for non-dedicated tankers, offshore operations and gas storage, and a high operational availability, even in severe weather. The near-shore facility comprises a single point-moored discharge point, a regasification unit and a storage facility.

The design work done to date shows the transfer system, regasification and storage options are fully feasible. The design is independent of the volumes of gas desired and the geographic location. Although it is new, all of its components are proven and have been used in terminal and offshore loading systems for some time.

LNG Pumps

LNG pumps sufficient to boost the pressure of the ship's discharge from about 50psi to cavern injection pressures of 2,000psi to 2,200psi have been contemplated by the major cryogenic pump-makers and cross no technological barriers from pumps widely used. Such pumps, however, have not yet been constructed and tested to industry's satisfaction. Unloading rates between 283 Mcf/hr and 353 Mcf/hr can be achieved with multiple pumps and are the design basis for the research design facilities.

LNG Heat Exchangers

Conventional designs of heat exchangers can be utilized to warm the resultant high-pressure LNG, but capacity limitations and energy consumption dictated a new approach resulting in the patented Bishop Process Heat Exchanger.

The Bishop Process warms LNG using a heat exchanger and stores the resulting dense phase natural gas in a salt cavern, discharges it to a pipeline or both. The heat exchangers use seawater as the warmant. The combination of the high-efficiency heat exchanger and the inherently energy-efficient storage operation using salt caverns indicate the total energy consumption in a salt cavern-based terminal would be equal to about 0.35% of the throughput volumes compared with as much as 3.0% in a conventional tank-based terminal.

To accomplish heat exchange in a horizontal flow configuration such as the Bishop Process, it is important the cold fluid be at a temperature and pressure such that it is maintained in the dense or critical phase so no phase change takes place in the cold fluid during its warming to the desired temperature. The dense or critical phase is defined as the state of a fluid when it is outside the two-phase envelope of the pressure-temperature phase diagram for the fluid. In this condition, there is no distinction between liquid and gas, and density changes on warming are gradual with no change in phase. This allows the heat exchanger of the Bishop Process to reduce or avoid stratification, cavitation and vapor

lock, which are problems with two-phase gas-liquid flows.

The effect of confining the fluid to the dense phase is illustrated by an analysis of the densimetric Froude Number, F , that defines flow regimes for layered or stratified flows:

$$F = V \left(gD \frac{\Delta\gamma}{\gamma} \right)^{-\left(\frac{1}{2}\right)}$$

Here, V is fluid velocity, g is acceleration due to gravity, D is the pipe diameter, γ is the fluid density and $\Delta\gamma$ is the change in fluid density. If F is large, the terms involving stratification in the governing equation of fluid motion drop out of the equation. As a practical example, two-phase flows in enclosed systems generally lose all stratification when the Froude Number rises to a range from 1 to 2. In this application, the value of the Froude Number ranges in the hundreds, which assures complete mixing of any density variations. These high values are assured by the fact that in dense phase flow, the term $\Delta\gamma/\gamma$ in the equation above is small.

Measurement of the Froude Number occurs downstream of the high-pressure pump systems and in the heat exchangers. Process simulations using a computer program and the finite element modeling conducted as part of the research project indicate the heat exchange occurs as predicted, icing is controlled and energy consumption for the system is significantly lower than experienced in conventional liquid tank terminals. Field tests to confirm the mathematical representations are expected to be performed.

Salt Formations and Storage Location

The Liberty LNG Terminal described in the research uses two existing salt caverns that have been solution-mined in a salt formation in Calcasieu Parish, La., capable of holding 16 Bcf of natural gas or the equivalent of cargo from about six ships.

The Vermilion 179 site would require the mining of caverns in an existing salt formation located about 1,000ft below the seabed. This case study locates the salt cavern storage facility in Vermilion Block 179, a well-known salt formation in water about 100ft deep. This is sufficient for the drafts of any known and contemplated LNG carrier. The rights to develop a salt cavern storage facility in U.S. territorial waters are obtained via lease from the U.S. Minerals Management Service. Such a lease would be granted on a “non-interference basis” with any existing or future mineral exploration and production lease on the same blocks. This research describes the development of six caverns, each initially of 2 million-bbl capacity but maintaining a wash string in operation so that while in operation and during time they could be continually washed to greater capacities, depending on the needs of the operator. These caverns could hold about 12 Bcf of dense phase natural gas at 2,000psi and could be developed and placed in operation in 12 months. They could



Figure 3: The Vermilion site would connect to the three largest offshore gathering systems in the Gulf of Mexico, Bluewater, SeaRobin and Texas Eastern, and have takeaway capacity in excess of 2 Bcf/d.

subsequently be enlarged to 4 million bbl each for a total storage capacity of 24 Bcf at a subsequent additional cost of less than \$2 million.

There are more than 1,000 salt caverns being used in the United States and Canada to store hydrocarbons. Storage in salt caverns exceeds 1.2 billion bbl of hydrogen, natural gas, natural gas liquids, olefins, refined products and crude oil. In the United States, the salt cavern storage sites form a logistical connection between the gas, gas liquids, refining and petrochemical industries. The entire inventory of the Strategic Petroleum Reserve, more than 600 million bbl of crude oil, is contained in salt caverns.

Salt caverns have high send-out capacity, are very secure, and very inexpensive to create and maintain compared with surface tanks, particularly cryogenic tanks. A difference between the operation of salt caverns used in LNG-receiving and conventional natural gas storage is the high rates of injection into the caverns compared with most facilities. Conventional natural gas storage in salt caverns uses compressors to boost the pressure of inlet gas to cavern injection at rates generally between 500 MMcf/d and 1 Bcf/d. This application would involve injections at 3 Bcf/d to 4 Bcf/d, which is accommodated by multiple caverns and well design. A significant energy savings occurs in pumping LNG compared with compressing natural gas. A geomechanical temperature and rock mechanics analysis conducted as part of the research project indicates that injections to the caverns and withdrawals from them at the design rates described are within salt tolerances.

The Pipelines

The Liberty LNG Terminal would connect to seven major natural gas pipelines having a takeaway capacity of 3 Bcf/d. The Vermilion site would connect to the three largest offshore gathering systems in the Gulf of Mexico, Bluewater,

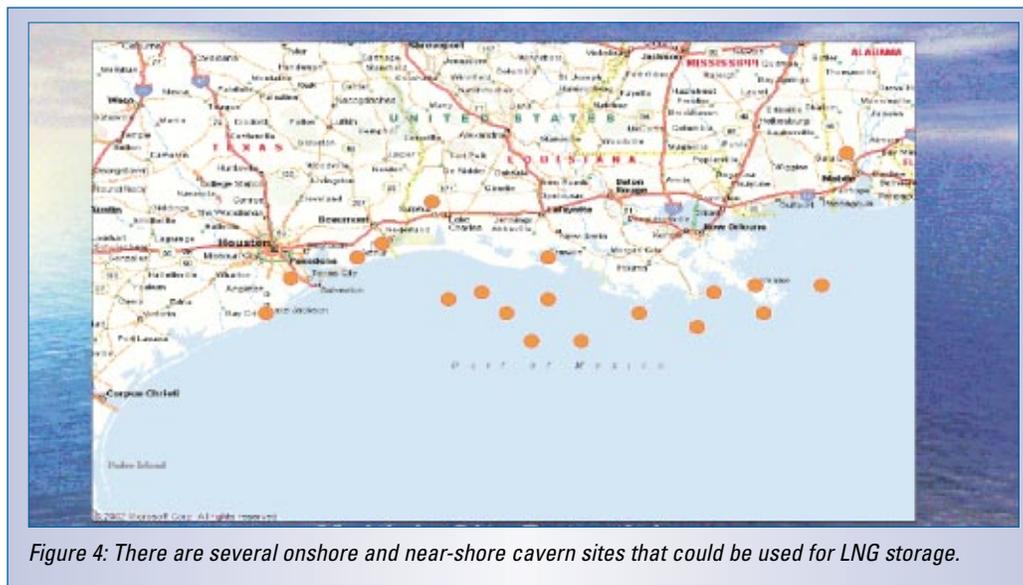


Figure 4: There are several onshore and near-shore cavern sites that could be used for LNG storage.

SeaRobin and Texas Eastern, and have takeaway capacity in excess of 2 Bcf/day (Figure 3). More than 20 additional sites were evaluated that combine salt formations suitable for storage cavern development in proximity to existing pipeline capacity, indicating that multiple locations could be developed to accept virtually any level of LNG imports that could be required in the future (Figure 4).

Facility Operations

The LNG ship mooring at the Liberty Terminal would be identical to that used at a conventional tank terminal. The offshore Vermilion 179 terminal would use a mooring and offloading system that has been designed for safe offshore loading/unloading of LNG to and from non-dedicated LNG carriers in wave heights up to 15ft and flow rates up to 353 Mcf/hr. All LNG ships are equipped to offload LNG cargo with shipboard pumps at about 50psi and -260°F.

At unloading however, rather than direct the LNG to surface tanks for storage, the ship's discharged LNG would be boosted by high-pressure LNG pumps to about 2,000psi to the heat exchangers. Seawater heat exchangers would warm the natural gas to design temperatures of 40°F. From the discharge of the heat exchangers, all low-temperature

considerations end, and the gas is transported in conditions standard to the natural gas pipeline industry.

The natural gas would be injected directly into the caverns and/or the connecting pipelines with appropriate pressure control as necessary. The entire cargo would be handled this one time, leaving only enough LNG on site to keep the pumps cold.

The operation of the salt cavern storage caverns, their maintenance and inspection would be identical to those practices in the 100-plus natural gas storage caverns in operation in North America and Europe.

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Process Engineering for Natural Gas Treatment using Direct-Injection H₂S Scavengers

By Kevin S. Fisher, *CrystaTech, Inc.*; and Dennis Leppin, Raj Palla and Dr. Aqil Jamal, *GTI E&P and Gas Processing Group.*

Design, troubleshooting and optimization of direct-injection H₂S scavenging systems pose many challenges. GTI and others from the oil and gas industry are working together to develop engineering test data and modeling software needed to effectively address these tasks.

Natural gas producers, domestically and abroad, have increasingly targeted lower-quality gas resources for development. This trend continues to drive the industry to search for better, more cost-effective and environmentally acceptable methods for treating sour gas. For economic reasons, hydrogen sulfide (H₂S) scavenging has emerged as the technology of choice for gas with low H₂S concentrations, for example, less than 200 ppmv.

Operators frequently select the direct-injection method of applying H₂S scavengers because of the lower capital

costs and/or the severe restrictions on space and weight encountered with offshore applications. While the direct-injection method offers these advantages over batch application of liquid or solid scavenging agents in large tower contactors, the ability to predict the performance of the direct-injection system or achieve treatment specifications without excessive chemical usage is frequently a challenge. For these reasons, Gas Technology Institute (GTI) and others in the industry have directed research during the past decade to develop an improved understanding of the fundamental mechanisms control-

ling the direct-injection scavenging process. The potential benefit of such an effort is substantial, considering the estimated \$50 million/year spent on H₂S scavenging chemicals in the United States alone.

H₂S scavenging research has been conducted primarily by independent research organizations such as GTI, product development groups within H₂S scavenging agent manufacturing companies or companies that use the products to treat their gas. For example, a group of several companies involved in North Sea gas production sponsored a project to develop a better understanding of

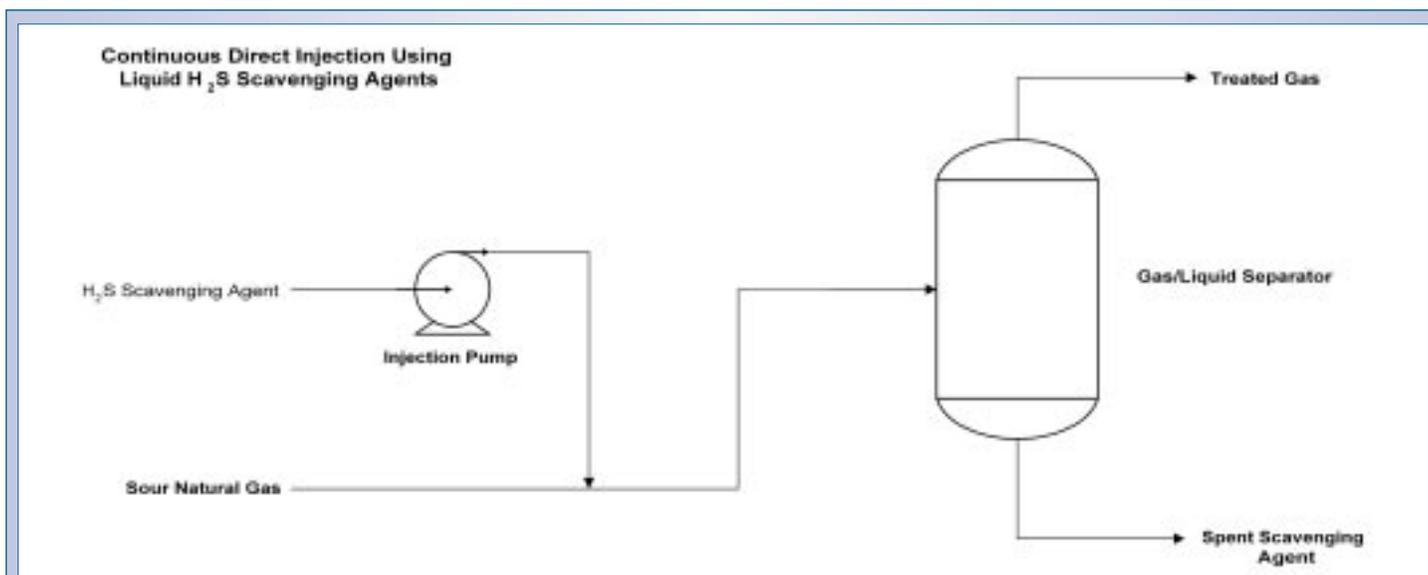


Figure 1: The basic direct-injection scavenging installation consists of a chemical injection pump, a means of introducing the scavenging agent into the natural gas pipeline, a length of pipe to allow for gas/liquid contact, and a downstream device for separating spent or excess scavenging agent from the gas.

how scavenging applications might be made more efficient. As a follow-up to this proprietary work, GTI, on behalf of three gas producer companies, began a joint-industry project (JIP) in 2001 to gather specific engineering test data to develop a software package to improve techniques for designing, troubleshooting and optimizing H₂S scavenging systems. This package expands on the capabilities of an existing GTI software product, *Scavenger CalcBase*[™] (GRI-96/0482), developed to allow rapid screening of H₂S scavengers for particular applications. The first phase of the JIP project will be completed in 2003.

This article provides an overview of the issues faced when designing or optimizing direct-injection scavenging systems and describes GTI's collaboration with the industry to develop test data and modeling software to support these activities.

How is Natural Gas Treated using Direct-Injection H₂S Scavenging?

Method of Application—Continuous direct-injection of scavenging agents into a natural gas pipeline is usually applied near the wellhead (after separation from produced water and hydrocarbons) or at centralized treating facilities prior to dehydration. The basic direct-injection scavenging installation consists of a chemical injection pump, a means of introducing the scavenging agent into the natural gas pipeline, a length of pipe to allow for gas/liquid contact and a downstream device for separating spent or excess scavenging agent from the gas (Figure 1). Piping tees, quills or atomization nozzles are used to introduce the scavenging agent into the pipeline. Atomization nozzles enhance mixing when gas velocities are low. While static mixers have been used to enhance gas/liquid contact, test data from GTI's test loop in South Texas have raised questions about the benefit of using static mixers for this application.

However, for situations where contact time is relatively short, some benefit may result from advanced contacting devices. Scavenging liquids may be partially removed downstream using gravity separators and/or coalescing filter/separators. For facilities with existing sparged-tower contactors, some operators may prefer to fill the towers with water and use them to remove spent scavenging agent from the treated gas, effectively polishing the gas and increasing the efficiency of the system.

Economics—The economics of treating natural gas with nonregenerable scavengers strongly depends on the concentration of H₂S in the gas stream. For relatively low concentrations, capital cost becomes the dominant factor, favoring continuous direct-injection applications over the more expensive tower-based method of application. As H₂S concentration increases, the scavenging agent cost becomes dominant, favoring solid-based agents that, in many cases, have lower costs per pound of sulfur removed.

For preliminary analyses, scavenger-treating costs can be estimated using published data. GTI's *Scavenger CalcBase* program provides a method for quickly estimating capital and operating costs for several H₂S scavenging processes. The program is intended primarily for initial screening of processes using algorithms based on design equations provided by scavenger vendors.

Other important factors include project life, seasonal operations, installation location (offshore vs. onshore) and spent scavenger disposal costs. A short economic project life or seasonal operations tend to penalize technologies with

higher capital costs because there are fewer standard cubic feet of natural gas to amortize the capital, and therefore costs per standard cubic feet are higher. As a result, direct-injection scavenging becomes more favorable for these operations because of the lower capital costs. For example, direct-injection scavenging has been used to successfully treat slightly sour gas (10 ppmv to 20 ppmv H₂S) from underground natural gas storage systems that operate for only 4 months during the year.

When gas must be treated offshore, equipment size and weight greatly affect treatment costs. The large size and weight of tower contactors largely makes them prohibitive for offshore operations, leaving only the direct-injection option. In addition to the size and weight limitations, the handling of spent scavenger becomes more difficult offshore. All these factors tend to favor the use of liquid scavenging agents in a direct-injection configuration for offshore application. In some cases, spent liquid scavenger can be blended with produced water and disposed of via injection wells or discharged to the sea after treatment.

The cost for disposal of spent scavenging agent varies widely depending on how these wastes are regulated by the governing authorities. In some cases, the spent scavenging agents must be handled and disposed of as a hazardous waste, greatly increasing disposal costs. A careful study of applicable regulations for a particular site location is an important part of the scavenger-selection process. It should also be noted that while scavenging agents themselves

A careful study of applicable regulations for a particular site location is an important part of the scavenger-selection process.

may not be hazardous, the spent scavenging agent could become hazardous because of the concentration of contaminants such as benzene or mercury removed from the gas.

Gas Stream Characteristics—Most H₂S scavenging agents are designed to treat gas over a wide range of pressure, temperature, composition and flow conditions. However, several gas stream characteristics should be evaluated carefully during the process design phase.

- **Water saturation**—Natural gas is usually treated before being dehydrated; however, it is sometimes necessary to treat a dry gas using scavenging agents, for example, at a terminal handling offshore production being brought ashore through a sour gas line to avoid platform processing. Water-based scavenging agents, such as solutions of triazine and iron oxide-based scavenging agents, generally require the gas to be saturated with water to prevent formation of unwanted solid by-products and to achieve the required H₂S level.
- **Oxygen content**—Oxygen is usually not present in natural gas unless gas is collected from wells under a partial vacuum. In these systems, oxygen sometimes leaks into the gas and may cause the formation of elemental sulfur in beds of iron oxide-based scavenging agents, resulting in a higher than normal pressure drop across the bed. Oxygen may also cause the formation of corrosive nitrogen dioxide when a nitrite-based scavenger is used.
- **Temperature**—Low-temperature gas can cause scavenger reaction kinetics to slow down and affect system performance. High temperature can cause the scavenger to break down and form corrosive products.
- **Pressure**—H₂S scavenging is more difficult at low pressures because the partial pressure of H₂S is lower for a given concentration and because

pipes and contactor vessels are generally larger in size.

- **Variations in flow rate**—Direct-injection systems are vulnerable to changes in flow rate. The H₂S removal performance drops off severely as flow rate (and thus gas velocity) is reduced. Tower-based contactors allow for better turndown of gas flow rates. GTI patented a contactor in 2000 for direct-injection applications whereby the turndown ability is improved to allow operation over a large range (e.g., a factor of ten or better) of gas flow rates.
- **Onshore vs. Offshore**—For onshore applications, providing adequate length of pipe to promote good conversion of the scavenger and to reach H₂S outlet specifications is usually not difficult. For offshore operations, adequate pipe length is usually not available, and it may be necessary to treat high temperature gas after a compressor.

Environmental and Safety Considerations—Numerous federal, state and local regulations in the United States and similar governing authorities in many other countries regulate the disposal of spent scavenger material. In addition to varying by jurisdiction, the regulatory requirements depend on the scavenging agent selected and the levels of other potentially hazardous components present in the natural gas stream.

All sour natural gas treating processes share the common hazards (fire, explosion and worker exposure to H₂S) associated with handling high-pressure combustible gases containing toxic levels of H₂S. In addition to these areas of concern, other potential hazards associated with the use of H₂S scavenging agents include eye and respiratory irritation; benzene, formaldehyde and toxic metals exposure; and height and confined space entry hazards.

Formaldehyde and caustic are not used much because of the related health and safety problems. Similarly,

the use of iron-sponge has declined during the years, in part because of the pyrophoric nature of the spent scavenging agent.

For direct-injection scavenging systems, the potential for exposure to toxic materials is highest during maintenance operations or when handling spent scavenger material. Pump repairs, change-out of atomization nozzles, or repair and maintenance of spent-scavenger handling equipment are operations that have the potential for exposure. During these times, high levels of volatile organic compounds may be present, and operators have more potential of coming into direct contact with a scavenging agent or the spent scavenger material.

Process design considerations—Many factors, including some site-specific, require careful consideration during the process design for a particular direct-injection H₂S scavenging system. The following discussion provides a checklist of several items that need to be addressed during the process design.

Inlet and Outlet Knockout Separators—Vendors of H₂S scavenging agents frequently recommend the use of an inlet knockout separator to remove water and/or free hydrocarbon liquids from the gas before treatment. The presence of excess free liquids has the potential to increase scavenger usage and treatment costs because of the additional scavenger required to react with the H₂S present in these liquids. Outlet knockouts usually are recommended to prevent entrained liquid droplets from reaching downstream glycol dehydrators or other process equipment that could be adversely affected.

Length of Pipe for Contact—The length of pipe available for gas/liquid contacting in direct-injection applications is an important design parameter. In general, longer pipe lengths result in improved H₂S removal and reduced chemical consumption.

Atomization—The importance of atomizing the scavenging agent as it is

injected varies by application. When gas velocities are low, pipe lengths are short, or when large pipe diameters are used, atomization can significantly improve performance. In other situations where long pipe lengths are available and gas velocities are high, atomization has little or no effect.

Water Saturation—Water addition is sometimes required if the gas is not saturated with water at the temperature and pressure where scavenging treatment is applied. This situation sometimes occurs when gas is heated before treatment or when previously dehydrated gas is present in the feed sour gas. In the case of triazine-based liquid scavengers, the reaction products are intended to stay dissolved in the spent scavenger, where they are ultimately separated from the gas stream for disposal. However, if the gas is subsaturated with water, enough water may evaporate from the scavenger solution to cause unwanted precipitation of solid reaction products in the pipeline. Some operators operate a small water injection pump upstream to add the required amount of water to saturate the gas.

Scale Inhibition—The formation of scale is a consideration when hard water may contact highly alkaline scavenging agent formulations. This may occur if the scavenging agent is diluted with water before use or if hard water is injected to maintain water saturation. In other cases, the spent scavenger may be commingled with other sources of hard water in downstream separators and produced water facilities.

CO₂ Interference—Carbon dioxide (CO₂) does not normally present a major problem because the most commonly used H₂S scavengers react selectively with H₂S. However, CO₂ is known to react at least partially with triazine-based scavengers and does compete for the scavenging chemical. In these cases, chemical consumption may be increased as a result of high levels of CO₂.

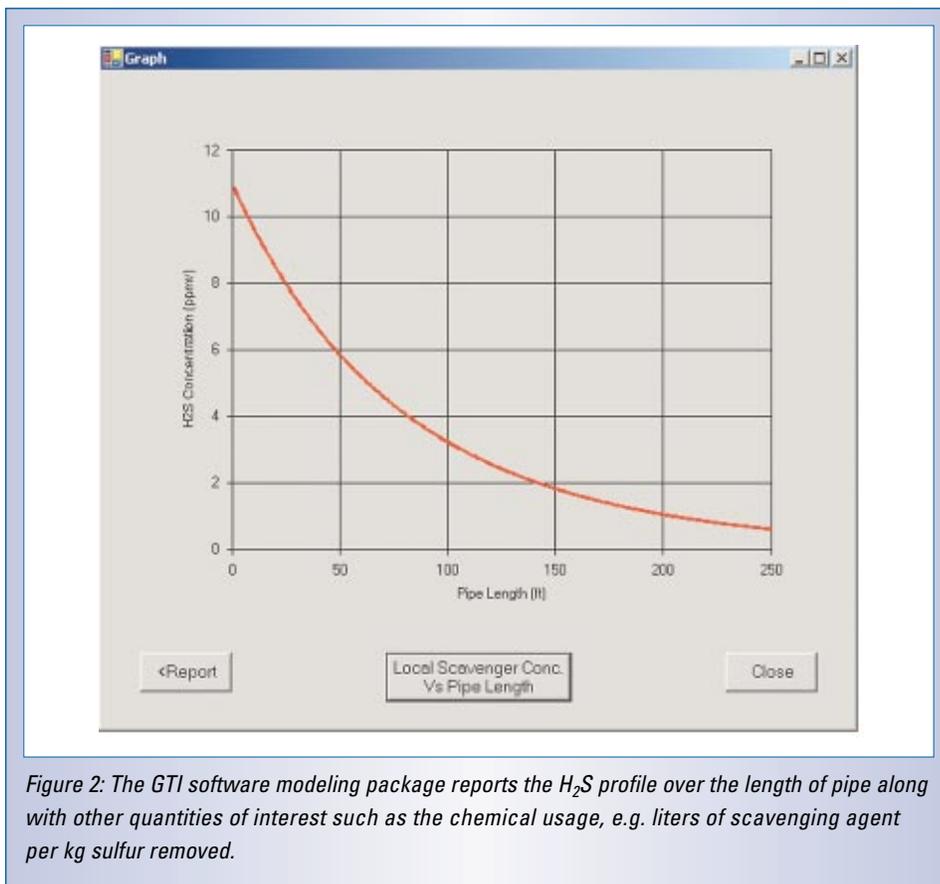


Figure 2: The GTI software modeling package reports the H₂S profile over the length of pipe along with other quantities of interest such as the chemical usage, e.g. liters of scavenging agent per kg sulfur removed.

GTI and Industry Sponsors Develop New Process Modeling Software

GTI, acting on behalf of JIP participants, is developing a new software-modeling package to make process calculations for direct-injection H₂S scavenging systems. In 1998, GTI published a set of equations largely based on empirical correlation of field data that could be used for direct-injection systems. The new model being developed is more mechanistic in nature and is based on rigorous modeling of the two-phase flow hydraulics, mass transfer and chemical kinetics. Further, the new model will be incorporated into a user-friendly program with a graphical user interface. The program will not be made available to the general public but will be available to the JIP participants and potentially to other parties expressing interest in it.

Theoretical models of the direct-injection process require knowledge of the following:

- reaction stoichiometry and kinetics between H₂S, CO₂ and the scavenging agent
- physical solubility of H₂S in the scavenger solution
- liquid- and gas-film mass transfer coefficients
- interfacial surface area available for mass transfer.

Once the above quantities are known, the H₂S absorption can be calculated based on the following mass balance equation, which is at the core of the new model:

$$\frac{d\gamma_{H_2S}}{dz} = \frac{-K_G a P \gamma_{H_2S}}{G} = f(z)$$

where

γ_{H_2S} = Mole fraction H₂S in the gas phase

G = Molar gas velocity, lbmol/hr/ft²

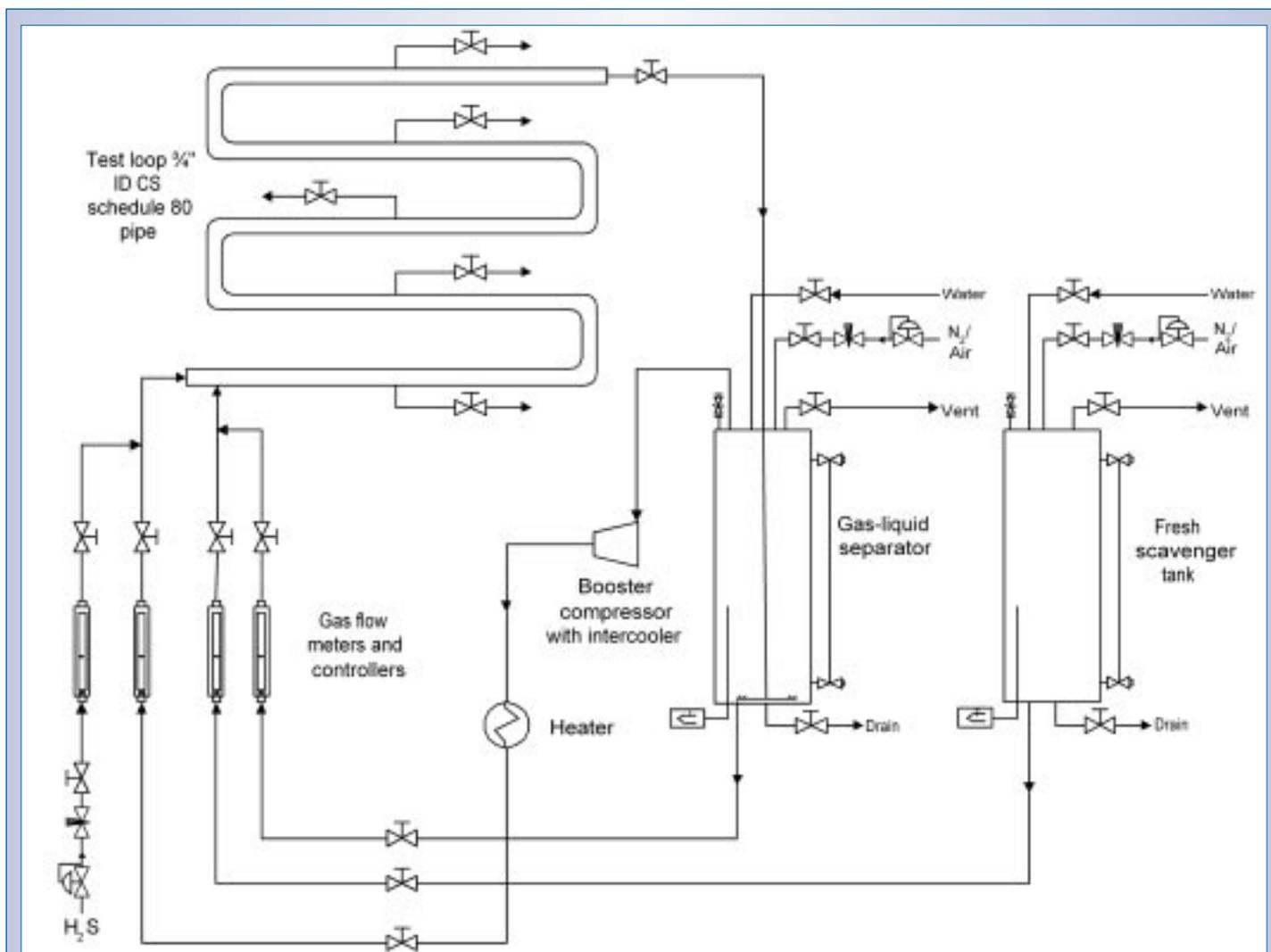


Figure 3: This diagram shows the design of the laboratory direct injection test rig commissioned in June.

z = Pipe length, ft

K_G = Overall mass transfer coefficient, lbmol/hr/ft²/atm

a = Interfacial area for mass transfer, ft²/ft³

P = Pressure, atm

This equation is a first-order linear ordinary differential equation and can be solved using standard numerical techniques (for example, a fourth-order Runge-Kutta method) as long as the function $f(z)$ can be evaluated at each point in the pipe. Evaluation of $f(z)$ requires an estimation of the interfacial area, gas and liquid mass transfer

coefficients, and enhancement factors used to describe the enhancement of mass transfer in the liquid phase because of rapid chemical reactions taking place in the diffusion film near the gas-liquid interface.

The model solves these equations and reports the H₂S profile over the length of pipe (Figure 2) along with other quantities of interest such as the chemical usage, for example, liters of scavenging agent per kilogram of sulfur removed. A full report of all intermediate quantities such as mean droplet size, interfacial areas, gas and liquid film coefficients, kinetic rate coefficients, etc., also is available.

GTI Constructs High-Pressure Test Flow Loop in Des Plaines Laboratory Facility

GTI is in the process of constructing a laboratory direct-injection test rig to study H₂S scavenging of natural gas under controlled conditions. A schematic diagram of the laboratory test rig is shown in Figure 3. This setup is made of schedule 80 carbon steel pipe with total contact length of 240ft. The entire structure is housed inside a 20-ft x 12-ft fume hood equipped with a carbon adsorption bed. The unit has a maximum gas flow of 0.6 MMscf/d under once-through



Figure 4: Construction of the negative pressure chamber is already complete.

and recycled flow conditions at temperatures up to 319°F and pressures up to 1,100 psig.

During a typical test, pure methane or nitrogen gas will be mixed with appropriate amounts of pure H₂S gas and the mixture will be continuously fed to the system and metered. The scavenger will be fed from a pressurized tank in lieu of pumps and metered using a rotameter. The scavenger will be injected into the pipe loop using a small nipple, quill or atomization nozzle from a pressurized storage tank. Gas-sampling taps are provided at convenient intervals. The gas and liquid exits the system and enters a separator. The gas then proceeds to a booster compressor, which compresses the gas back up to inlet pressure. Any additional components to achieve the desired composition are added back to the gas. The spent liquid will be sent to

disposal, recycled and/or sampled as necessary. This unit will allow GTI to collect significantly more data under a wider variety of conditions and more precisely control the test conditions.

The purchase of various equipment items such as compressor, gas-liquid separator, heater, cooler, carbon beds and storage vessel is complete. The construction of the negative pressure chamber (Figure 4) and compressor room are completed and the work on building the pipe loop is underway. The setup is scheduled to be commissioned by the end of June 2003.

GTI Offers Services for Testing of New Scavenging Agents and/or New Mass Transfer Devices

GTI is set up to carry out research projects related to H₂S scavenging for interested parties. The staff involved in these projects

is experienced in field operations and certified regarding H₂S safety. Through the course of the various scavenger projects GTI has been involved in during the past decade, the organization has amassed a large database on direct-injection scavenging that has proved useful for design and troubleshooting of applications. In late 2003, GTI will be offering participation opportunities in a follow-up JIP to the current program that has focused on developing a model for direct injection scavenging. Testing new scavengers and contactor devices in the new testing system at Des Plaines, Ill., as well as in the field system in McAllen, Texas, and improving the computer model are all on the table for the program work scope, which the participants will finalize. GTI also is interested in carrying out projects directly for clients. Recent work has included design of direct-injection scavenging installations based on the GTI patent at storage field installations, and field-testing of proprietary scavengers is

being discussed with several clients. GTI continues to offer and support the GTI Scavenger CalcBase program for tower applications of scavengers and will develop a commercial version of the direct injection model in the future. ♦

For more information on GTI gas processing products and services, or to join the JIP described in this article, please contact Dennis Leppin at GTI. Portions of this article were reproduced from an earlier GasTIPS article from the Fall of 2000. For a complete listing of published test data, literature references and related information, the reader is referred to Fundamentals of H₂S Scavenging for Treatment of Natural Gas, by Fisher et. al., published in the proceedings of the Ninth GRI Sulfur Recovery Conference, 1999. Additional detailed information on scavenging has been compiled in the collected proceedings of the GRI Small-Scale Sulfur Recovery Conferences, GRI-00/0085.

Consortium Selects 13 New Projects to Aid Stripper Well Operators

By Gary Covatch, NETL

The recent war with Iraq reminded Americans of the need for the United States to become less dependent on foreign energy sources.

Reducing the dependency on overseas countries would require finding new resources, but it would also need to include maintaining production from wells producing in the United States. Because many of the oil and gas fields in this country are mature, the production from these wells has declined and will continue to do so. Sooner or later, most of these wells will fall into the stripper well category.

A stripper well is defined as a well that produces less than 10 b/d of oil or less than 60 Mcf/d of gas. Numbers released by the Interstate Oil and Gas Compact Commission for 2001 show there are 403,459 stripper oils wells in the United States producing an average of 2.15 b/d of oil and 234,507 stripper gas wells producing an average of 15.8 Mcf/d (IOGCC 2002). Stripper wells operate on the lower edge of profitability and because of that, when wells owned by majors reach that level of production, these companies usually sell them to small independent operators with lower overhead or more regionally-specific portfolios. These wells are very important to the energy security of the United States, as they represent 15% of the oil and 7% of the gas produced. However, continued production from these wells is increasingly dependent on new technologies, which will keep them economical.

Recognizing that most stripper wells are operated by smaller independent operators that have neither the funds nor the staff to develop new technologies, the U.S. Department of Energy through the National Energy

Technology Laboratory (NETL) developed and sponsors the Stripper Well Consortium (SWC). The SWC offers operators across the United States a forum to discuss with technology developers the operating problems they face in their daily operations.

The operators play an integral part in developing and selecting projects for funding, assuring the relevance and timeliness of the research. A presentation of each proposal is provided to the SWC members, which allows all members to ask questions and comment on the proposed work. The actual selection of projects is made by the Executive Council, which is comprised of seven elected members from the SWC membership.

The SWC held its third annual meeting May 5-6, 2003, in Pearl River, NY, where 27 proposed research projects were presented and reviewed for possible SWC funding. Of these, 10 proposals were accepted for full funding and three proposals for partial funding (Table 1). A total of \$1.156 million was committed by the SWC for the co-funding of these 13 projects. A brief description of each of the projects selected for 2003 is provided below.

The SWC has provided \$2.25 million in co-funding to support a total of 26 projects in its first 2 years. All the first-year projects have been completed and are scheduled to be released to the SWC in June 2003. The second-year projects are nearing completion. A brief description of the projects funded in 2001 and 2002 as well as additional information about the SWC is available on the SWC Web site at www.energy.psu.edu/swc.

Field Testing of the Vortex Oil and Gas Unit for Downhole Applications – Vortex Flow LLC

In 2002, Vortex Flow was awarded a grant by the SWC to research, design and lab-test a downhole tool using the patented and patent-pending vortex technology. The technology takes a disorganized single or multi-phase flow and transforms it to a spiral flow with an associated boundary layer that runs along the inside wall of the pipe. The vortex flow created by the technology reduces the friction that causes pressure drops as fluids (gas or liquids) flow through a pipe. The object of applying the technology in a downhole setting is the reduction of pressure drops in a tubing string. Initial tests have shown the tool has the potential to reduce pressure drops in tubing strings, thus increasing production of gas and oil in low-flowrate stripper wells.

Several tool designs were manufactured and later tested at Texas A&M University. Initial tests results indicated the final tool design reduced the pressure drop up the tubing string and reduced the required gas flow needed to lift liquids up the wellbore.

The objective of this project is to field-test the tool developed in the 2002 project. In this project, eight downhole tools will be installed in operating wells and the production data collected, analyzed and compared with pre-tool production data to determine the tool's effectiveness. The ability to transfer the Vortex technology to a downhole application will allow for greater technology leverage and will provide a simple

means of improving production from many operating stripper wells.

Chamber Lift—A Technology for Producing Stripper Oil Wells: Stage II – The Pennsylvania State University

Arguably, the largest expense with the operation of most stripper oil wells and many stripper gas wells is the lifting costs associated with the removal of fluid from the wellbore. The predominant artificial lift method used is rod pumping. Much of the equipment is outdated

and the maintenance costs large and increasing. The problem the operator faces is how to upgrade the production systems at low enough capital cost that the typical well can show a reasonable economic return on investment.

In 2001, the SWC funded the development of a chamber lift system as an alternative to existing lifting technologies. The concept of the system is that gas is injected into the oil column via a small-diameter tubing string set in the production tubing. This gas then displaces the accumulated fluid to the surface via the

annular space between the injection string and the production string. The process is controlled using a sensor and motor valve at the surface.

The project was broken down into three phases: a laboratory prototype, a field test and a computer modeling of the process. To date, the laboratory studies have been completed with synthetic oil and begun with field crude. Field tests have demonstrated the feasibility of the technique and the computer modeling of the process begun. This project is a continuation of the 2001 project in which additional laboratory tests with

Project Topic:	Organization
<i>Field Testing of the Vortex Oil and Gas Unit for Downhole Applications</i>	Vortex Flow LLC
<i>Chamber Lift – A Technology For Producing Stripper Oil Wells – Stage II</i>	The Pennsylvania State University (Penn State)
<i>Low Cost Wireless Communications-Based Pressure and Temperatures Gauge for Production Optimization Applications</i>	Tube Technologies
<i>Design and Construction of a Low Cost Portable Oil/Water Production Testing Unit</i>	Advanced Resources International
<i>Produced Water Treatment: Developing a Project to Market a Program to Allow the Sale of Treated Oilfield-Produced Brine for Beneficial Use</i>	Texas A&M University
<i>Building and Testing a New Type of Compressor for Stripper Well Production Application</i>	W&W Vacuum & Compressors Inc.
<i>Plunger Conveyed Chemical System for Plunger Lift Wells</i>	Composite Engineers
<i>Enhanced Real-Time Propellant Activation During Downhole-Mixed Fracture Stimulation Process for Low-Permeability Stripper Wells</i>	ReatimeZone Inc.
<i>Pressure-Volume-Temperature Study of the Interaction of Nitrogen and Crude Oil</i>	Penn State
<i>Sonication Stimulation of Stripper Well Production in East Gilbertown Field, West-Central Alabama</i>	Tech Savants Inc.
<i>Restimulation of Three Under-Stimulated Shallow Gas Wells Coupled with the Installation of Pumping Equipment to Accelerate Post-Stimulation Fluid Removal</i>	Lenape Resources (partially funded)
<i>Locating the End of Tubing for Efficient Production of Gas</i>	Colorado School of Mines (partially funded)
<i>Modification of the GOAL PetroPump for Open-hole Applications</i>	Brandywine Energy & Development Co. (partially funded)

Table 1: Projects Selected for Funding by SWC in 2003.



Stripper wells are important to U.S. energy security, representing 15% of the oil and 7% of the gas produced.

field crude will be performed as well as computer modeling and additional field tests necessary to define its applicability.

Low-Cost Wireless Communications-Based Pressure and Temperatures Gauge for Production Optimization Applications – Tubel Technologies

Hydrocarbon producers are faced with significant challenges to maintain a well's operational and production cost-effectiveness because of large changes in electricity rates in different parts of the United States, volatility of oil and gas prices, and unexpected requirements for intervention in the wells. Optimization of the processes required to produce hydrocarbons constitutes an ongoing concern in the oil and gas industry. The

goal of this project is to develop a low-cost gauge based on an existing commercial high-end wireless gauge developed by Tubel Technologies to monitor pump performance, monitor fluid level to optimize lifting operation and to lower lifting costs, and monitor bottomhole pressure to optimize drawdown and for buildup tests. The buildup tests will provide reservoir pressure information for the optimization of the hydrocarbon production.

This project will research, develop and test a lower-cost, high-reliability, real-time wireless gauge composed of compressional acoustic waves-based wireless communications transmitting data in real time. The data will be transmitted through the production tubing, strain gauge pressure sensor and a temperature sensor for measurements of downhole pressure and temperature, as well

as a surface module to acquire the transmitted signal from downhole and process the data. The new wireless gauge can be deployed anywhere in a production and injection well. The gauge will utilize low-power electronics and sensor technology to acquire and process in real time well data related to production and formation parameters. A battery pack will provide power for operation of the system downhole, and the battery operational life is expected to be in excess of 5 years.

Design and Construction of a Low Cost Portable Oil/Water Production Testing Unit – Advanced Resources International

There are many marginal waterflood plays operated around the country, such as Oak Resources Inc.'s properties in Carter

County, Okla. As a matter of course, routine production testing of all wells is a standard practice necessary for obtaining oil-water production ratios. However, standard low-cost methods often lead to erroneous measurements because of low sampling frequency and the non-homogeneity of the production fluids. This non-homogeneity often occurs because of variations in the production stream related to the flow regime and its composition. Although production testing units are available with the capability of increased sampling frequency, thereby reducing the error because of fluid homogeneity (increased sampling in shorter time frames yields a significantly more representative composition), these units can be cost-prohibitive (up to \$50,000) to the marginal oil operator. As a result, the operator often must sacrifice accuracy for cost savings.

To meet this need, the Advanced Resources International project team will conduct a thorough review of possible unit components, highlighting their advantages with regard to cost and reliability. This will culminate in a design recommendation to Oak Resources Inc., which will critically review the design prior to prototype construction. Field-testing will be concerned with sampling production streams from about 30 oil wells with the new unit as well as the units employed by Oak Resources.

Restimulation of Three Under-Stimulated Shallow Gas Wells Coupled with the Installation of Pumping Equipment to Accelerate Post-Stimulation Fluid Removal – Lenape Resources

Tens of thousands of gas wells were completed in the Appalachian basin in the 1970s and 1980s. The majority of these wells were completed using the so-called “limited entry” perforation technique – a limited number of perforation spread out over hundreds of feet of a target interval – coupled with a hydraulic fracture

stimulation, which utilized proppant concentrations that current technology considers inadequate. This limited entry technique often resulted in uncertain fracture geometry and a range of results. After completion, standard practice fluid recovery operations normally resulted in the majority of completion fluid remaining in the wellbore/fracture years after the initial completion. As a result, a large number of wells exist that have only produced a small fraction (often less than 20%) of the originally estimated gas-in-place with conservative drainage estimates. Such wells may generally be identified by their ability to build shut-in well head pressure to within 75% to 80% of original shut-in pressure, yet they may exhibit a very low flow rate soon after the initiation of production.

In an effort to demonstrate these reserves are economically recoverable, Lenape Resources will re-stimulate three shallow gas wells in its Lakeshore field, Chautauqua County, NY. The following steps will be performed as part of the project:

- perforate a selected small (10ft to 15ft) pay interval with a high perforation density (four shots/foot)
- pump a hydraulic fracture treatment containing about 60,000 lb of proppant at a maximum final sand concentration of at least 6 lb/gal of fluid
- immediately install pumping equipment with surface facilities sufficient to handle increased fluid volumes
- collect production data and report results to SWC.

Locating the End of Tubing for Efficient Production of Gas – Colorado School of Mines

Removal of water and hydrocarbon liquids from gas wells is increasingly recognized as an important topic for low-permeability gas reservoirs. A key factor is the location of the end of tubing (EOT) in the casing relative to the various gas-bearing formations that have been completed. If not removed, liquids in the casing will cause two detrimental consequences. First, the backpressure of accumulated water on the perforations causes decreased production rate. Second, back-flow of water from the casing through the perforations to the formations can produce a “water block” that prevents gas flow. There is little agreement in the engineering community on the appropriate location for the EOT.

To address this problem, the Colorado School of Mines will conduct a literature search on the technology and begin concept development for future model development for properly locating the end of tubing for effective production of gas. The work also will include flow loop testing.

Produced Water Treatment: Developing a Project to Market a Program to Allow the Sale of Treated Oilfield-Produced Brine for Beneficial Use – Texas A&M University

A public/private/academic partnership led by Texas A&M University has been created to identify mechanisms to pay for the treatment costs incurred in desalination of oil field brine. This project will

A public/private/academic partnership led by Texas A&M University has been created to identify mechanisms to pay for the treatment costs incurred in desalination of oil field brine.

demonstrate that an unconventional source of fresh water can be obtained by produced water treatment/desalination to provide fresh water for beneficial use. This unconventional source of fresh water can then be used for industrial purposes to substitute for scarce fresh water resources planned for community water needs. The value of this new resource makes it important to encourage oil and gas operators to institute such practices where practical.

This partnership consists of the academic researchers at Texas A&M University, manufacturer Tarlton Supply, oil and gas producer Burlington Resources and the staff at the Texas Railroad Commission. Tests will be conducted at the Burlington Resources facility supporting their drilling operations in the Barnett Shale play in North Texas. Water produced from fracturing will be treated. Once treated, the fracturing fluids can then be re-used for subsequent well operations. This eliminates the need for transporting fresh water from the Trinity River and the need to haul recovered brine to offsite disposal wells. It is expected that this cost savings in water handling plus the value of the fresh water resources saved by re-use will be sufficient to pay for brine treatment/desalination. Estimates show more than 40 million gal of fresh water could be saved in the Fort Worth Basin alone.

In 2001, the SWC funded Texas A&M efforts to remove regulatory roadblocks preventing beneficial use of treated produced water. The regulatory agency in Texas for the oil and gas industry (Texas Railroad Commission) recently has issued a

letter endorsing the A&M program and pledging to work with local and state agencies to implement projects.

The project's objectives are:

- to identify market mechanisms that provide incentives to those willing to pay the costs of developing this new and unconventional source of fresh water
- to demonstrate treatment/desalination of oil field wastewater for re-use.

New technology used to process the water produced with oil and gas operations removes impurities and creates a fresh water resource that can be used for beneficial purposes. The project will consist of short- and long-term field testing with full-size process trains to gather operations data on the desalination process. This information will then be used to present the case for underwriting the costs of this treatment.

Modification of the GOAL PetroPump for Open-hole Applications – Brandywine Energy & Development Co.

During the past 2 decades within the Appalachian Basin, several tens of thousands of shallow oil and gas wells (100ft to 300ft) have been completed using open-hole techniques with multiple notched, fractured and produced zones. These wells are often configured with 7-in. to 8⁵/₈-in. steel casing cemented through the water table aquifers, then open rock hole wellbore (6¹/₄-in. to 7⁷/₈-in.) to the total depth of the well. These wells follow a similar production performance history as their predecessor-cased wells, that history being several months of

flush production followed by decreasing well pressure and yield of oil and gas. These wells, like many others, fall within a relatively short period into the category of stripper well production. Downhole pressure in these wells declines to a point where the well is no longer able to lift the fluid in an unassisted manner to the surface. Often in these multi-zone completion wells, an uphole zone will act as a thief for downhole higher-pressure producing zones, further complicating their operation and production. In ongoing stripper well production from these wells, beam pumps, tubing velocity strings, tubing and plungers, and other conventional techniques often are employed with some finite success. Most of these techniques do not allow the well to produce itself down (gas and oil) to something close to the formation pressure. The net result of this is non-captured reserves and higher operation cost for gas and oil produced.

The objectives of this project are to perform the engineering design required to apply the unique operational efficiencies of the GOAL PetroPump with state-of-the-art reworking of openhole oil and gas wells. This project will build upon the successful results of previous projects in which the GOAL PetroPump was developed for cased holes. The GOAL PetroPump is an elegant solution for the automatic lifting of fluids from oil and gas stripper wells. The simple design of the tool's onboard valve control allows it to free-travel within the wellbore, accumulating a predetermined volume of fluid above the tool, closing the self-actuating valve and delivering that fluid to the surface. The tool is "smart" in both directions, dropping downhole when pressure at the wellhead is low or reduced by downhole fluid accumulation. The tool is smart uphole as well, using below-tool formation pressure to lift the tool and fluid (oil/brine) to the surface, subsequently free-floating in the wellhead lubricator and allowing downhole pressure/gas to flow to the process unit. At such time as pressure

New technology used to process the water produced with oil and gas operations removes impurities and creates a fresh water resource that can be used for beneficial purposes.

has declined below tool control pressure, the tool drops once again, repeating the automatic pumping cycle.

Testing of the GOAL PetroPump Tool under an existing SWC project in cased-perforated stripper wells has demonstrated 1½- to three-fold improved production at a fraction of the service necessary to operate other stripper well operating systems. The current tool is designed to operate in downhole conditions of brine, oil, gas and condensate under rigorous in-well chemical and pressure conditions. The tool will operate in well conditions with pressure ranges of 30psi to 600psi, lifting 0.1 bbl to 40.0 bbl of fluid per tool cycle for 4½-in. cased wells.

Building and Testing a New Type of Compressor for Stripper Well Production Application – W&W Vacuum & Compressors Inc.

A novel type of variable capacity compressor has been developed to solve compressor problems encountered in low deliverability gas production operations. The Weatherbee Positive Displacement Compressor/Vacuum Pump, a patented device, has the largest volume displacement-to-size ratio of any device in the world. The spherical geometry design provides the largest internal volume-to-surface area ratio possible so that with each 360° revolution almost all of its internal volume is displaced.

The Weatherbee Pump also has a unique design feature in its capacity control mechanism, which allows the rate of the device to be changed to meet increased or decreased demands without increasing the rotations per minute of the input shaft. This volume control feature works like a throttle on an engine; set on high it can easily handle high volumes, and by throttling back the mechanism, volumes are reduced, thereby saving on energy usage and operating costs. This device uses only the energy

necessary to compress the amount of gas the well is actually producing. This capacity control feature is a major selling point for a majority of applications. The ease of sizing makes one pump appropriate for various volume requirements. This feature will be particularly beneficial to applications where compression requirements fluctuate or where volume can only be estimated and may vary drastically, as in gas well compression.

The Weatherbee Pump provides the following advantages as compared to existing products of similar output capacities:

- substantially reduced size and weight
- the versatility of the volume control mechanism
- reduced energy requirements
- less maintenance and lowered operating costs
- ability to operate the pump with input shaft turning either clockwise or counter-clockwise
- ability to reverse the direction of flow without disconnecting the pump or changing rotational direction of the input shaft
- ability to perform a dual function similar to one-half motor and one-half pump/compressor.

The objectives of this project will be to evaluate the new compressor concept by constructing a model and testing it in a controlled environment. Once the prototype model has been proven, it is expected an additional project will be undertaken to test the pump in a field application.

Plunger Conveyed Chemical System for Plunger Lift Wells – Composite Engineers

As more demand is placed on the aging gas wells in the United States, there is a need to better preserve the integrity of these wellbores. Many deep, marginal gas wells have been sold off to smaller independents that cannot afford to replace tubing strings, repair casing leaks or even add packers to patch these older wells. Without mechanical failures, these wells will continue to produce gas for years. Research suggests 87% of plunger lift wells fail because of mechanical failures, such as holes in tubing and/or casing. These problems are mostly because of corrosion and aggravated tubing wear from plunger/tubing abrasion. In the past, many attempts have been made to apply chemicals to plunger lift system with little success.

In this project, a simple and inexpensive chemical plunger lift system will be developed and field-tested. It is projected only simple modifications will be required for the plunger lubricator cap and plunger. Both components can be swapped out on existing systems with common tools in less than an hour, typically. It is believed the proposed system modification will preserve the integrity of the wellbore mechanics and in some cases extend a well's ability to produce at a lower gas-to-liquids ratio based on today's common ratio calculations. Scale, paraffin, hydrogen sulfide, etc., can be treated on a continuous basis with this system.

The Weatherbee Pump also has a unique design feature in its capacity control mechanism, which allows the rate of the device to be changed to meet increased or decreased demands without increasing the rotations per minute of the input shaft.

Enhanced Real-Time Propellant Activation During Downhole-Mixed Fracture Stimulation Process for Low-Permeability Stripper Wells – ReatimeZone, Inc.

The objective of this project is to develop and demonstrate enhanced reservoir stimulation processes for stripper wells. Proprietary and previously untested experimental processes will be tested that utilize a novel, chemically induced *in situ* fracturing process combined with hydraulic fracturing stimulation.

One process includes the downhole blending of a mixture of propellants and various activator agents or oxidizers, which are pumped separately (and safely) for reaction and generation of secondary fracturing energy in the hydraulically induced reservoir fracture. The propellants may be safely pumped down the casing for later staged admixture with oxidizers to generate an energy release in the near wellbore and formation fractures, concurrent with hydraulic fracturing. Thus, secondary fractures are generated to augment the primary induced fractures created by hydraulic fracturing. Theoretically this process should result in significantly greater fracture length extension and enhanced hydrocarbon flow to the wellbore.

The proposed admixture of propellants and oxidizers, including encapsulated or time-delay propellants and activators, occurs concurrent with ReatimeZone's patented downhole-mixed stimulation process, whereby one stimulation component is pumped down the casing while the second stimulation fluid (gases and/or proppants may be included in either fluid) is pumped down the tubing and blended downhole. A second activated propellant fracturing approach includes pumping a

propellant-laden fluid into the reservoir fractures and then subsequently pumping a second oxidizer-laden fluid into said fractures, with the option of pumping a fluid separation pad as deemed necessary by the operator. This simple well completion system is safe and easily utilized at the wellsite and will enable dramatic improvements in reserve recovery efficiency, safety, cost savings and overall reservoir fracturing success in terms of obtaining extended fracture propagation. The field tests for this project will be performed in the Permian Basin.

PVT Study of the Interaction of Nitrogen and Crude Oil – The Pennsylvania State University

Membrane-generated nitrogen has several applications in the oil field. It is commonly used in energized fluid drilling and workovers, and in secondary and tertiary recovery projects. The nitrogen created using membrane technology is non-reagent grade and contains oxygen as its principal contaminant. The amount of oxygen generated in the separation process varies from near-zero mole percent to as high as 5 mole percent and is a function of adjustment to operating parameters of the equipment. However, the reality of the process is that the lower the amount of oxygen in terms of mole percent, the lower the volume of gas generated. In most field operations, the operators attempt to generate the maximum volume of gas the physical conditions permit. Limitations generally are from increased corrosion of tubular goods and/or the increased tendency for the formation of emulsions in produced fluids.

Therefore, the objective of this project is to develop a fundamental understanding of

the phase behavior of nitrogen-oxygen gases in the presence of hydrocarbons. To accomplish this, extensive laboratory tests will be conducted using a conventional PVT apparatus. In order to generalize the results of these experiments, the resulting data will be used to develop a computer program characterization of these fluids in the presence of oil. The need for this generalization is to provide to the producer a tool that would permit the design and optimization of the projects involving these fluids.

Sonication Stimulation of Stripper Well Production in East Gilbertown Field, West-Central Alabama – Tech Savants Inc.

This project will evaluate the use of sonication as a stimulation tool in oil wells. Sonication energy, produced by converting electrical energy to mechanical energy, enters and moves laterally within the oil-bearing formation being stimulated, increasing the mobility of the oil through the addition of energy, by lowering the oil's viscosity and (perhaps) by cleaning the wellbore and perforations.

To demonstrate the effectiveness of using sonication to stimulate production, three field tests will be performed in the East Gilbertown field in west central Alabama using various combinations of power intensity and frequencies. Following each of the field tests is a 6-week period where the impacts of the test are evaluated in terms of increased production of oil and water, variations in production during time and the lateral extent of the impacted zone as reflected in nearby wells. The final report will contain all the data and test procedures, economic data, conclusions and recommendations. ♦

For more information, please contact author Gary Covatch at gary.covatch@netl.doe.gov, (304) 285-4589.

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The objective of the ReatimeZone, Inc. project is to develop and demonstrate enhanced reservoir stimulation processes for stripper wells.

Gas: A Messenger from Subsurface Resources

By Dr. Larry Cathles,
Cornell University

A detailed chemical and modeling analysis of a 77-mile by 124-mile area of the offshore Louisiana Gulf of Mexico shows how gas venting from deep sources alters shallower hydrocarbons and carries information that could guide exploration.

Clean-burning, energy-rich natural gas is an increasingly desirable hydrocarbon resource. Gas can be retained in a basin for hundreds of millions of years (as in the Anadarko) yet vents almost continuously in active basins such as the Gulf of Mexico Basin. Five years ago, the Gas Research Institute awarded a research contract to Cornell University to examine the way gas moves in the deeper portions of a very active basin. Could the capillary forces that arise when gas is present in grain-size layered sediments produce the very low permeability surfaces, called seals, that divide basin interiors into compartments of variable and often very high overpressure, and could this affect gas and hydrocarbon migration? Laboratory experiments reported from a previous GRI-funded study suggested this was possible (Shosa and Cathles, GCSSEPM, 2002). But could it be demonstrated in the field?

To be sure to catch all relevant processes, the GRI study cast its investigative net over a large (79-mile by 124-mile) area of the offshore Louisiana Gulf of Mexico (Figure 1). What was caught was not so much an improved understanding of seals, which is commented on only briefly in this article, but a clear view of unanticipated and possibly more important processes. The study discovered and documented the dramatic and systematic effects gas can have on oil through a process called gas washing. In the north of the study area, more than 90% by weight (wt%) of the n-alkanes in reservoir oil have been carried off by gas. The pattern of washing decreases in a regular fashion to zero in the southern end of the study area. Modeling shows this variation

is expected from the changing pattern of sediment deposition. Modeling also shows the gas washing and observed decrease in oleanane and increase in sulfur-bearing bensothiophenes to the south (the next clearest chemical trends in the study area) are possible only if very little petroleum is retained in migration conduits between the source and the surface. The washing seems to take place in the deepest sand in any area, for example, the first sand encountered by upward-migrating hydrocarbons. The analysis shows the petroleum system in the northern Gulf of Mexico is a flow-through system in which only about 10% of the petroleum that escapes from the source strata is retained in basin sediments and more than 90 wt% is vented into the ocean. The venting is happening today through hundreds of seafloor sites, and known reservoirs have been filled very recently. Therefore, the chemistry of the gas and washed oils carry information on the current pattern of subsurface petroleum migration relevant to exploration for subsurface hydrocarbon resources.

The Offshore Louisiana Study Area

Figure 1 shows a GoCAD image of the top of salt (gray surface with spiky salt domes) in the study area, which henceforth will be called the GRI Corridor, and stratigraphic layers from four sites where 3-D seismic data from the industry was acquired and interpreted. The stratigraphy, all chemical analyses, and selected physical and petroleum data are assembled in a

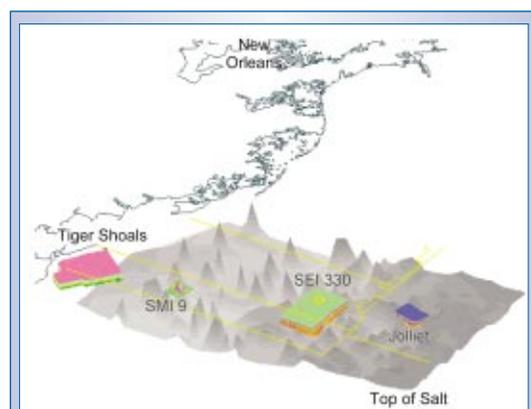


Figure 1: This figure shows the location of the GRI study corridor in the offshore Louisiana Gulf of Mexico Basin. The base is the top of salt compiled from 2-D seismic data. Strata interpreted from 3-D seismic data at four locations also are shown. SMI 9 is ChevronTexaco's South Marsh Island 9 salt piercement-related field, SEI 330 in Pennzoil's (Devon Oil) South Eugene Island Block 330 field, and the southernmost stratigraphic package contains ConocoPhillips' Jolliet field.

GoCAD project that is included with the six-volume final report available from GRI (GRI-03/0065). Corridor source rocks have a generative potential of 1,400 billion bbl of oil and 8,600 Tcf of gas; 2.6 billion bbl of oil and 45 Tcf of gas have been discovered. The top of overpressure (12 lb equivalent mudweight surface), determined from mudweight data in 2,131 wells, is a highly irregular, spiky surface that cuts thousands of feet across stratigraphy in many areas (Figure 2). Many, but not all, of the spikes are related to salt domes. Temperature gradients can change from about 65° to 76°F per 0.62 miles over distances of about 31 miles in a checkerboard pattern, which would dramatically affect hydrocarbon maturation.

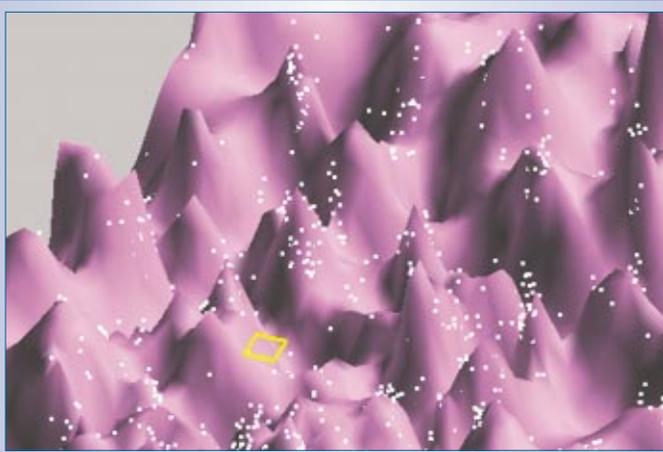


Figure 2: A subset of the data defines the 12 ppg equivalent pressure surface (white points) displayed against the krieged representation of the same 12-lb mud surface. The yellow square is South Eugene Island Block 330. The krieged surface represents the pressure data reasonably well but fails to capture the full height of the peaks.

Chemical analyses of 138 un-biodegraded oil samples show remarkably regular trends in gas washing (Figure 3) and source-related biomarker indices.

The spikes in the top of overpressure surface complicate relating this surface to hydrocarbon phase separation of a relatively constant composition petroleum. Leak zones appear to be localized

temperature distribution in the corridor is that expected. Local anomalies are partially related to salt and variations in sedimentation rate, but that is not their full explanation, and they remain enigmatic to some degree. Oil chemical variation turned out to be the most interesting, surprising and process-significant data.

in faults and shear zones bounding salt sheets and diapirs. Once established, they persist and become increasing methane-rich. Away from spikes, the top of overpressure surface could be a phase boundary, and its depth might be at least partly controlled by petroleum chemistry. Sufficient data to test this possibility was unable to be assembled. The temperature pattern is significant and interesting. The general

the n-alkanes has been removed by gas washing in the northern end of the Corridor (Tiger Shoals). All the oils there have break numbers of ~24 and show ~90 wt% oil removal. The washing intensity decreases in a reasonably regular fashion from north to south. No washing is observed at the south end of the Corridor. The chemistry of the Corridor oils is extensively discussed in the report cited above. After gas washing, the next most process-significant aspect of the oil chemistry is the clear presence of oleanane in the north but not in the south and a dramatic increase in sulfur-bearing benzothiophenes to the south. This result is interpreted to come from the maturation of two source beds: a carbonate Jurassic one that extends uniformly across the Corridor and a silicate Eocene one that extends across only the northern half of the Corridor. Eocene-sourced oils should contain oleanane, since their source is younger than mid-Cretaceous and plants containing oleanane had evolved, and should be sulfur-poor because iron from the shale will precipitate sulfur as pyrite in the source. Jurassic-sourced oils, on the other hand, should be sulfur-rich because carbonates contain insufficient iron to precipitate the sulfur as pyrite at their source and are too old to contain oleanane.

The importance of these observations becomes clear when the evolution of the Corridor is reconstructed and petroleum generation and migration modeled. The Jurassic source lies at about a 9-mile depth in the Corridor. Unless the petroleum retention in migration conduits above the source is less than ~0.5% of the pore space in the sediments, no petroleum can escape the surface. The migration fraction must be smaller than this because oil and gas are venting at hundreds of seafloor localities. For the oil to have an Eocene signature, such as containing oleanane and being sulfur-poor, the later-generated Eocene oil must displace the earlier-generated Jurassic oil.

temperature distribution in the corridor is that expected. Local anomalies are partially related to salt and variations in sedimentation rate, but that is not their full explanation, and they remain enigmatic to some degree. Oil chemical variation turned out to be the most interesting, surprising and process-significant data.

Hydrocarbon Chemistry

Gas washing is measured by comparing the mole fractions of n-alkanes in an oil with the distribution expected if the oil were unaltered. In unaltered oils, the mole fraction of n-alkanes decrease exponentially with carbon number, C_n . Figure 3 shows the n-alkane mole fractions in one Tiger Shoals oil peel off from the exponential trend at $n \sim 24$. The shaded zone is the missing oil. In this case, the missing oil represents about 90 wt% of the original $C_n > 10$ oil. The north-south profile in Figure 3 plots the n-alkane removal in 138 unbiodegraded oils cross the Corridor. More than 90 wt% of

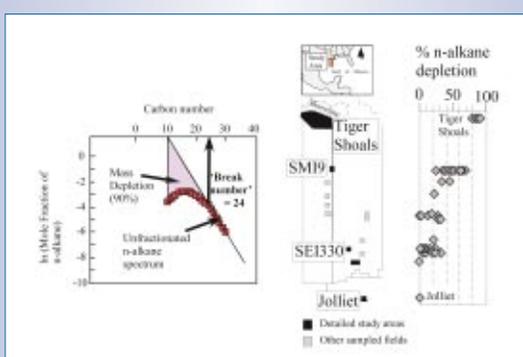


Figure 3: A total of 138 oils are analyzed for gas washing (left). The percent mass depletion of n-alkane components $\geq C_{10}$ is defined as the gap between an unaltered oil with exponentially decreasing n-alkane mole fractions and the sample oil (shaded area). The graph on the right shows the regular decrease in the percent of n-alkane mass removed by gas washing from north to south across the GRI Corridor.

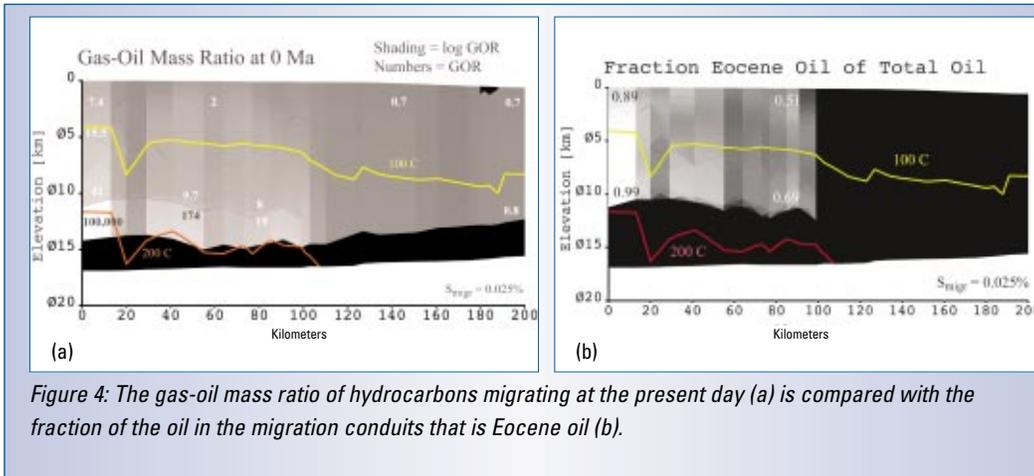


Figure 4: The gas-oil mass ratio of hydrocarbons migrating at the present day (a) is compared with the fraction of the oil in the migration conduits that is Eocene oil (b).

This is possible only if the migration pore fraction is less than $\sim 0.05\%$. If this is the case, all the chemistry fits nicely. Figure 4 shows at a migration pore fraction of 0.025% the oil at Tiger Shoals (in the north) is 89% Eocene and 51% Eocene in the middle of the Corridor. Furthermore, because the Jurassic source is now generating gas, the gas-oil ratio in the migrating hydrocarbons is high enough in the north and middle of the section (Figure 4b) to wash the Eocene oils as observed. For 90 wt% oil removal, about 4 lb of gas are required to wash each pound of oil. The migrating gas-oil ratio decreases to the south such that we expect no gas washing at the southern end of the Corridor, as observed.

A final matter of importance is that equation-of-state modeling of the washing process indicates that the break number (Figure 3) is a direct measure of the depth at which the oil is washed. Combining this with Corridor geology at the four sites where 3-D seismic data suggests the gas washing occurs in the deepest sand at any locality. Hydrocarbons can be delivered at the rate needed to fill known reservoirs as recently as geologically indicated if collected from areas ~ 10 miles to 12 miles in radius (the scale of the salt-withdrawal minibasins in the area). Gas and oil mix in the deepest sand, and the oil is washed there. The hydrocarbons then

escape at a few localities along the faulted margins of minibasins.

Conclusions and Implications

Oil chemistry requires the petroleum system in the northern Gulf of Mexico basin to be a flow-through system in which very little hydrocarbon is retained between the source and the surface, and almost all ($>90\%$) the petroleum that escapes its source vents into the ocean. About 30% more hydrocarbons than have been produced and consumed by humans throughout the entire petroleum era have vented into the ocean from the small Corridor. Admittedly, this occurred during a fairly long period of time (about 10 million years), but clearly humans and nature are promoting the same basic process (the venting of hydrocarbons).

Because so much gas is required to wash the oils as observed, the washing process reflects major aspects of the subsurface flow system. Overall, the pattern of washing in Figure 3 is regular, but significant variations in washing intensity occur in its mid-section. The variable washing in this area must reflect variations in flow and mixing in the migration conduits. For example, areas where oils are relatively intensely washed must connect to subsurface zones where gas is preferentially transmitted compared with oil, and

conversely areas where oils are comparatively unwashed must connect to migration pathways that transmit relatively little gas. Structures along major migration conduits will have a greater probability of being filled with hydrocarbons. Thus, analysis of the gas washing pattern could help guide exploration to structures more likely to be filled and more likely to be filled with oil or gas. Washing may have other economic implications. For example, washing may cause

asphaltenes to precipitate in the subsurface, and gas-washed oils may therefore be less prone to precipitate them in seafloor transmission pipes. \diamond

Acknowledgements

The Gas Research Institute (GRI) carried out this research at Cornell University, with a chemical analysis subcontract to The Woods Hole Oceanographic Institution also supported. Many researchers and students worked on the project during its lifetime. They are co-authors in the GRI report. Steven Losh and Mike Wizevich at Cornell, and Jean Whelan and Lorraine Eglinton at Woods Hole were the principal contributors to the work summarized here. Peter Meulbroek discovered and modeled gas washing of the type described in his Cornell Ph.D. dissertation. The author would also like to acknowledge the exceptionally able guidance and support of Robert Richard Parker, the GRI project manager for most of this project. Further information is available from the final report (which includes a GoCAD project and spreadsheets of all data), GRI-03/0065. Information is also available from the author, Lawrence M. Cathles, Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY 14853, (607) 255-2844, cathles@geology.cornell.edu; and Robert W. Siegfried, Associate Director Earth Sciences, Gas Technology Institute, (847) 768-0969, robert.siegfried@gastechnology.org.

Understanding the Mechanisms of Hydrate Nucleation and Inhibition

By Dr. Ram Sivaraman,
Gas Technology Institute

The Hydrates Flow Assurance Facility at Gas Technology Institute (GTI) provides tools for understanding the mechanisms by which hydrates form and grow.

Natural gas hydrates, which occur in permafrost and sub-sea sediments or in thick layers on the deepsea floor, are now considered as a potential energy source for the future. The U.S. Geological Survey estimated in 1995 that U.S. hydrate resources total about 320,000 Tcf. On the other hand, gas hydrates also can cause serious operational problems when they form “slugs” inside gas pipelines, plugging valves and other transport facilities.

Traditionally, methanol and glycols have been used by the industry to inhibit hydrate formation in pipelines. When these “thermodynamic inhibitors” are injected in very large quantities – 30 wt% to 60 wt% – they alter the chemical potential of the aqueous or hydrate phase and cause hydrate to dissociate (dissolve) at lower temperatures or higher pressures. However, use of thermodynamic inhibitors can cost \$60,000/d. There are some new-generation hydrate inhibitors described in the literature (*Kelland et al*; 1995), including, “kinetic inhibitors” (KI) and anti-agglomerants (AA). The inventors of these materials have made claims about their value, but the industry has largely continued to use methanol as an inhibitor. There is not yet sufficient confidence in new-generation inhibitors to warrant their wide use in deepwater field operations.

Kinetic inhibitors do not affect the thermodynamics of hydrate formation; instead, they delay hydrate nucleation and growth. They can be beneficial in some cases. Anti-agglomerants prevent

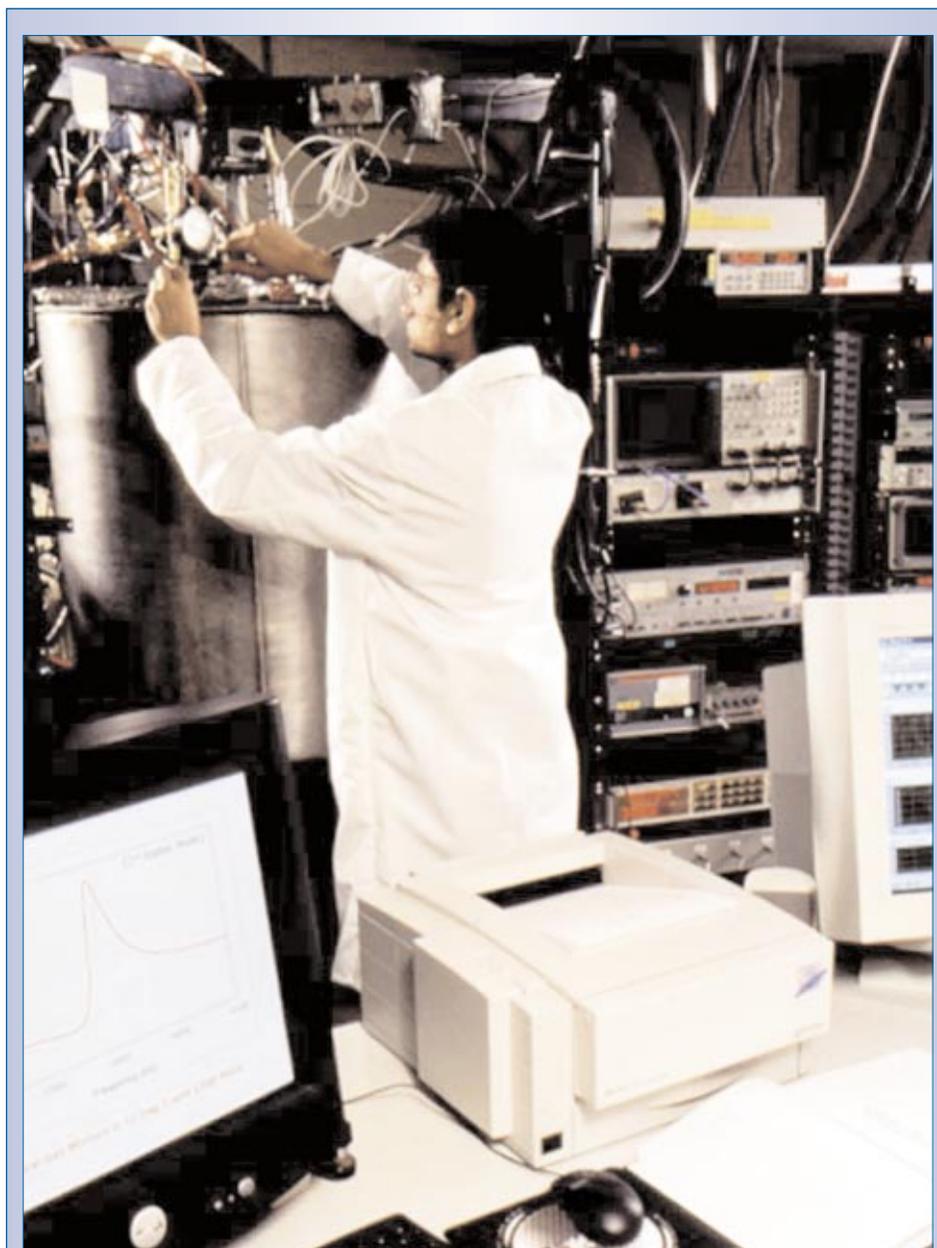


Figure 1: GTI Acoustic Resonance Spectrometer

the aggregation of hydrate crystals, which allow these tiny crystals to be pumped through a gas line or valve without plugging. Both can be effective at low concentrations.

Understanding the mechanisms of hydrate nucleation and formation will help improve knowledge of hydrate inhibition and can lead to development of efficient new inhibitors that can substantially reduce the costs of inhibitor treatment. GTI's Hydrate Flow Assurance Facility is equipped with state-of-the-art instrumentation and analytical equipment that can help the industry evaluate the potential benefits of various inhibitor treatment options.

GTI Research of the Impact of Low-Dosage Inhibitors (LDIs) on Hydrates

The solution to gas hydrate problems lies in the development of new-generation hydrate inhibitors. Industry prefers to use inhibitors at low-dosage levels in order to comply with stringent environmental regulations and control costs. GTI has developed a world class hydrate flow assurance facility equipped with state-of-the-art technologies in three laboratories at its corporate headquarters campus in Des Plaines, Ill. In this facility, GTI has proven capabilities for screening for the best low-dosage KI or AA and can help identify cost-effective inhibitors for use in deepsea pipeline operations.

An article published in the summer 2002 issue of *GasTIPS* described the broad use of laser imaging technology at GTI for hydrate management. The focus of this article is GTI research on the kinetics and mechanism of hydrate formation and dissociation, with and without inhibitors. GTI has a variety of acoustic (Figures 1-3) and calorimetric tools (Figures 8-9) for conducting this research and has used these tools to study the impact of thermodynamic inhibitors, KI and AA at various dosages on hydrates formation.

Laboratory Measurements

Acoustic Resonance Technology Update—Acoustic resonance technology

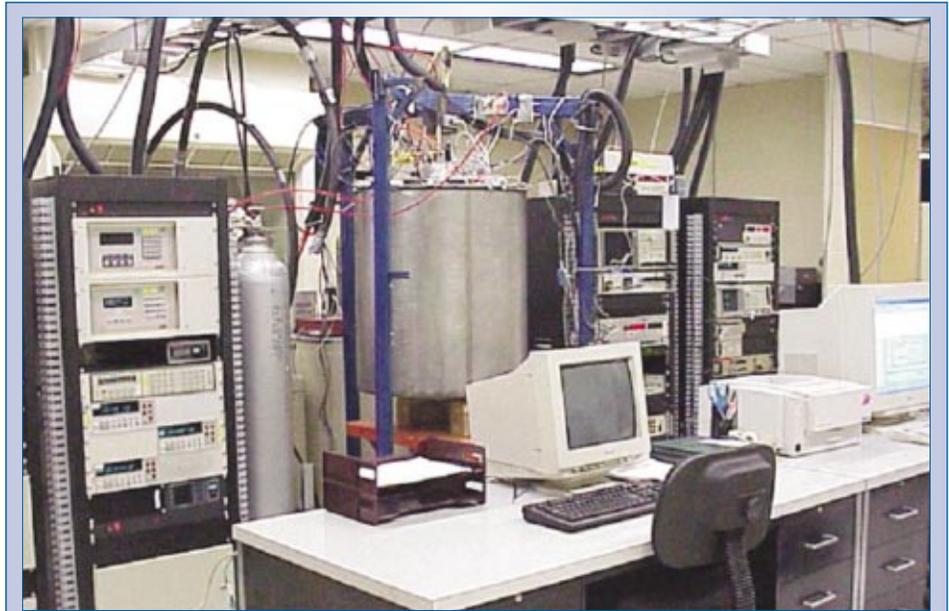


Figure 2: Acoustic Resonance Spectrometer control system.



Figure 3: Liquid nitrogen cooling system control.

offers powerful insights into many aspects of gas hydrates research. When acoustic waves are propagated through a gas mixture confined to a sphere at reservoir conditions, the signal output at the receiver carries all the changes it has gone through during the phase transition of the mixture and provides valuable information of hydrate onset and dissociation.

The high-speed digitization of acoustic spectra of a reservoir fluid, which has gone through hydrate phase transition, allows researchers to understand events that occur very rapidly. The acoustic technique is preferred for murky reservoir fluids that cannot be studied using optical techniques to detect hydrates onset. By analyzing the acoustic signatures,

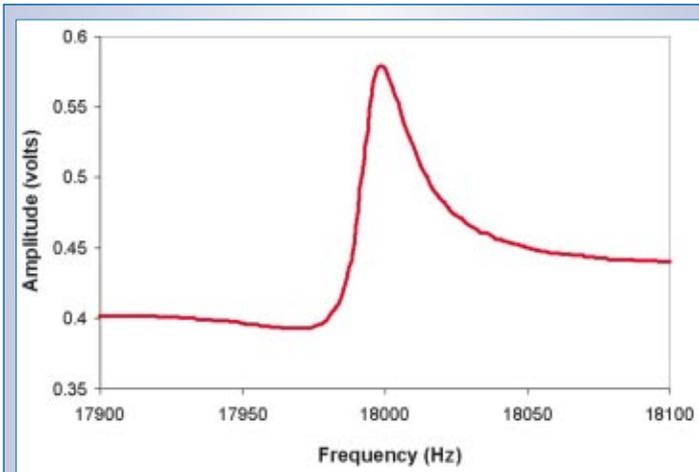


Figure 4: Second radial mode resonance frequency peak.

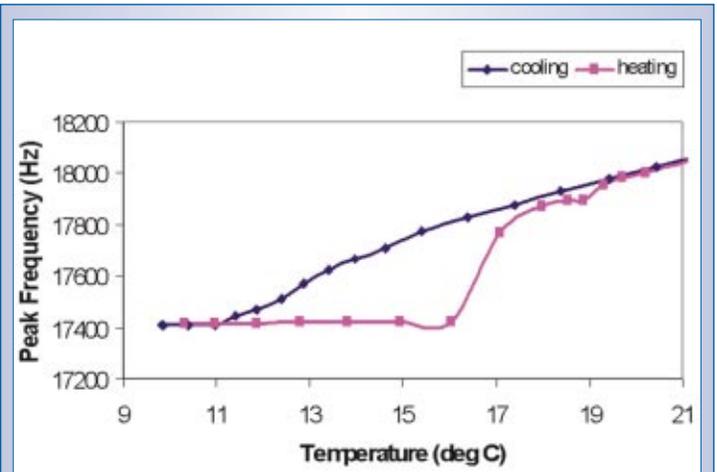


Figure 5: Acoustic determination of hysteresis of natural gas hydrate formation and dissociation.

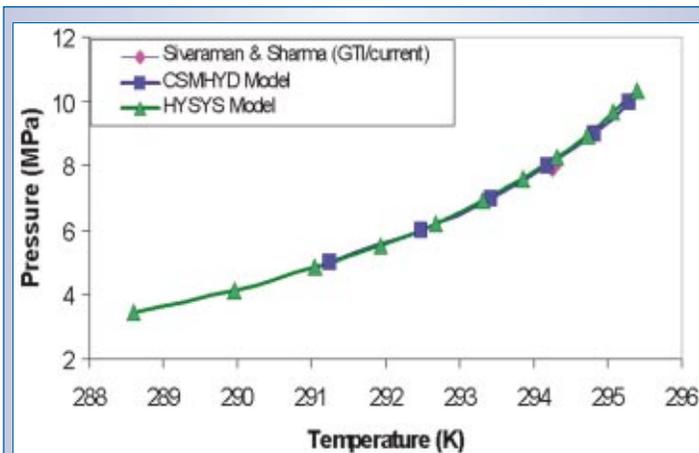


Figure 6: Comparison of current data for natural gas hydrate with models.

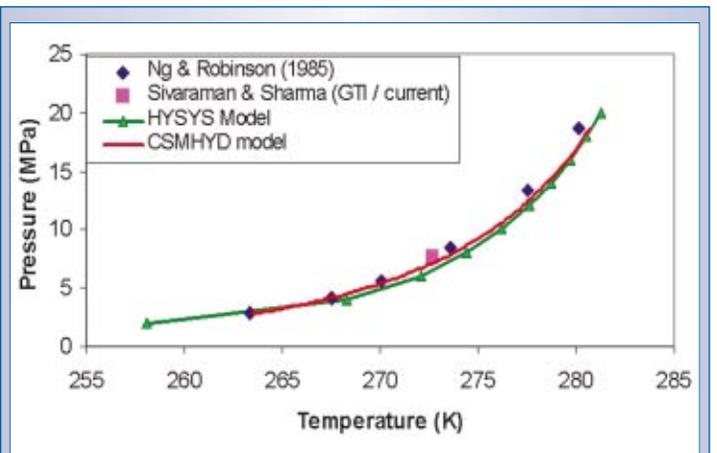


Figure 7: Comparison of current data for gas hydrate with 20 wt% methanol with literature data and models.

powerful insights into the evolution of the event may be realized. Acoustic data analysis can provide quantitative data valuable for developmental research.

The acoustic tool at GTI is an automated 25mm spherical acoustic resonance spectrometer developed for precision sonic speed measurements in live reservoir fluids. The system is capable of pressures of 0 to 42 megapascals (MPa) or 6,000 psia and has a temperature range of 450°Kelvin to 225°Kelvin. The heart of the system is a 25-mm sphere with two transducers. One transducer (transmitter) propagates acoustic waves

into the sphere in which the gas mixture is confined to the reservoir pressures. The second transducer (receiver) receives the acoustic signal that has gone through the phase changes along with the gas mixture when the temperature conditions were changed. The system is shown in Figures 1 through 3. The system control has a function generator that excites the transmitter through an amplified sine wave signal and generates acoustic waves inside the sphere. The signal received is amplified by a low-noise amplifier and then sent through a Lockin amplifier to pick out a clean

second radial mode (Figure 4) with a high signal-to-noise ratio. All this equipment is interfaced to the computer to control test operations and acquire data. The temperature is controlled by a proportional temperature controller and measured by a 100-ohm platinum resistance thermometer. The pressure is measured through a Ruska differential pressure gauge coupled with a pressure controller. Custom-made software has been developed at GTI and integrated with LabView.

The digital image of the radial mode signal is stored along with temperature

and pressure data. Because of the symmetry of the sphere, radial resonance modes prevail rather than the tangential modes. The second radial mode was identified and tracked during cooling and heating runs. The software tracks a selected radial resonance mode during the temperature changes of the sphere suspended in a vacuum-jacketed bath. The cooling and heating of the systems associated with the equipment have been modified to accommodate the dynamic measurement mode using liquid nitrogen heat exchange coils, fins and double-walled vacuumed stainless-steel jackets for better temperature control and low heat losses. Temperature and pressure measurements along with the radial mode frequencies are monitored in real time and recorded by the computer. The second radial mode resonance signal obtained for the natural gas mixture is shown in Figure 4. Figure 5 presents the hysteresis of natural gas hydrate formation and dissociation as determined from the acoustic data. The acoustic frequency vs. temperature trace is the replica of the sonic speed vs. temperature for the second radial mode from the following sonic speed relation for a gas confined in a sphere (Rayleigh, 1896; Moldover 1986):

$$v = \frac{2 \pi a f_{20}}{\gamma_{20}}$$

Where v is the sonic speed in meters/second, a is the radius of the sphere (25mm), f_{20} is the frequency of the second radial mode and γ_{20} is the respective eigen value (7.72525184) for the sphere. The sharp change in the frequency at the onset of hydrate phase transition is because of the sharp sonic speed change at the entrapment of natural gas by the water molecules to form hydrate crystals during the cooling process. During the heating process at the hydrate equilibrium temperature, the dissociation is completed and the mixture goes back to a single phase, confirmed by the overlap of the traces in Figure 5.

The hydrate onset was determined to be 51.73°F (10.96°C) at a frequency of 17,410Hz and a pressure of 1,154 psia, as shown in Figure 5. A close comparison of GTI laboratory results with literature data (Ng and Robinson, 1985) and various models (HYSYS, 2001, Sloan 1990) shows agreement (Figures 6-7) for a system without and with methanol thermodynamic inhibitor, respectively.

Calorimetric Measurements Update—GTI established calorimetric measurement capabilities at

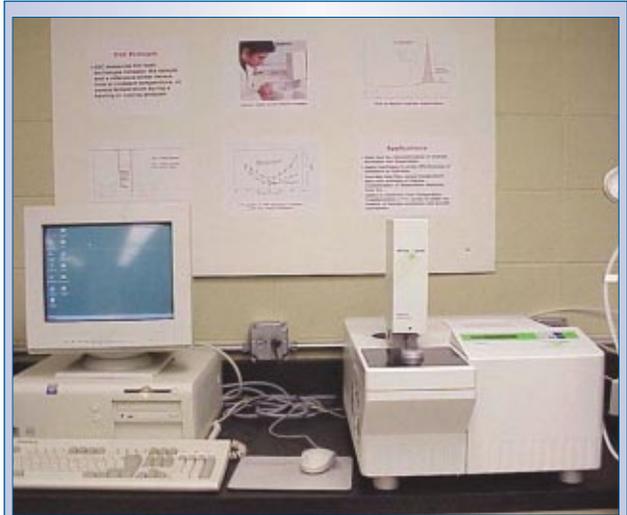


Figure 8: Differential Scanning Calorimeter at GTI flow assurance laboratory.



Figure 9: The robotic arm and sample tray assembly of the Differential Scanning Calorimeter.

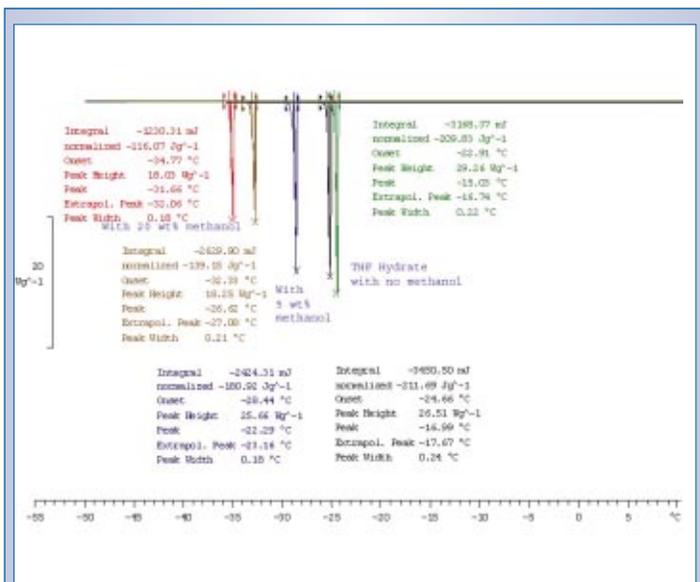


Figure 10: Comparison of low dosage methanol effects on tetra hydro furan hydrate.

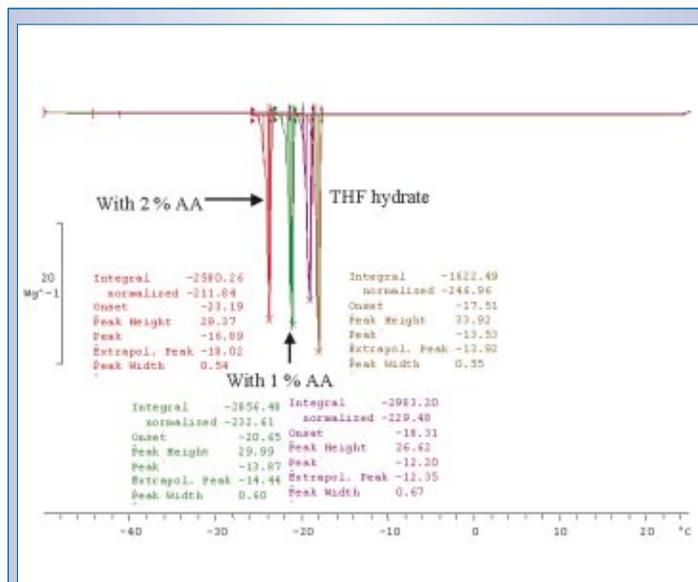


Figure 11: Comparison of the effects of a proprietary inhibitor on tetra hydro furan hydrate.

the GTI flow assurance facility for three reasons:

- cost-effective control of hydrate formation in subsea production and fluid-transportation networks, to provide an acceptable margin of safety for hydrate inhibition over a range of subsea conditions
- improved characterization of hydrates as an energy resource, based on research to improve hydrate detection capabilities and to better understand mechanisms of hydrate formation and dissociation in laboratory-formed hydrates representative of Gulf of Mexico hydrates
- the collection of heat capacity data for field samples from the Gulf of Mexico, Alaska and the Cascadian Margin.

The differential scanning calorimeter (DSC) is a powerful tool to examine the impact of inhibitors on the nucleation, growth and control of hydrates. It is of great value in determining the efficiency of various inhibitors in the control of hydrates at low dosages, information that could translate into millions of dollars for a producing company

because of safer drilling and increased gas production with minimum downtime. DSC measurements help researchers better understand how hydrates form and dissolve, leading to new tools that can help operators of pipelines and storage systems keep the gas flowing to customers and ensure the safety of gas-industry workers. Research results will also help the industry develop environmentally friendly and low-cost new inhibitors to control hydrates.

The calorimetric tool installed at the GTI flow assurance facility is a Mettler Toledo DSC 821 with a robotic arm assembly (Figure 8-9) that can handle about 35 samples in a single loading. Special high-pressure sample pans are used for field-sample heat-capacity measurements. The system was calibrated by melting pure indium and bismuth and by freezing pure water. Tetra hydro furan (THF) forms a Structure I hydrate similar to that of methane hydrate, so calorimetric study using the model THF hydrate system is analogous to the study of methane hydrate for all evaluation purposes. A predetermined amount of THF and water mixture (1:17)

samples were taken in the 10-mg to 15-mg range from all solutions and sealed in 40-µL aluminum crucibles. Then the crucibles were loaded in a robotic tray in a sequential order. Insertion temperature of samples was kept at 77°F (25°C). One by one, the samples were cooled to -58°F (-50°C) to form hydrate and then heated back to 77°F to dissociate the hydrate, at a 41°F (5°C)/min rate. The tests were repeated to get concordant values. Heat flow vs. temperature and time were recorded for each sample. A trace analysis program was used to evaluate onset and dissociation temperature of THF-water hydrate from the heat flow vs. temperature data for samples with and without inhibitor. The results were analyzed to evaluate the impact of inhibitors in controlling hydrate. A close comparison was made of the efficiency of methanol, polyvinyl pyrrolidone, polyvinyl caprolactam and an anti-agglomerant (at different and low dosages) on Structure I THF hydrate (Figures 10 and 11). The results indicated that 20% methanol was able to suppress the onset of crystallization by 60.8°F (16°C). However, 1% of PVCap was able to suppress the hydrate

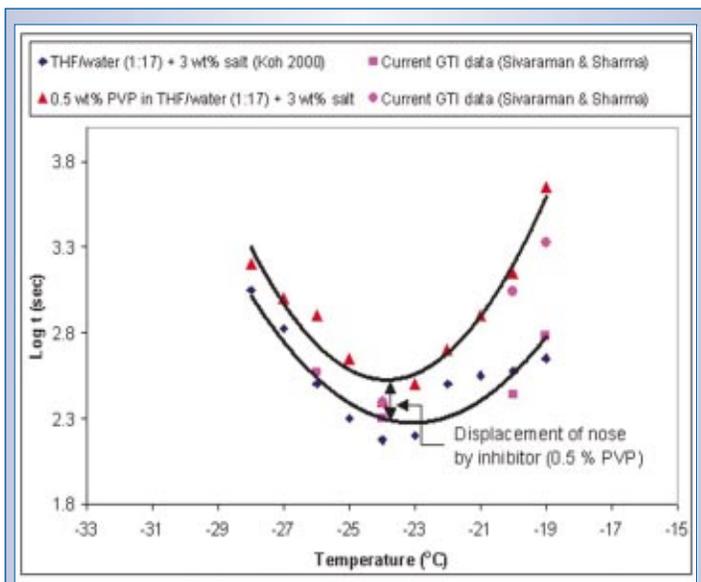


Figure 12: Time temperature transformation curves comparison of the effects of PVP inhibitor on nucleation of tetra hydro furan hydrate.

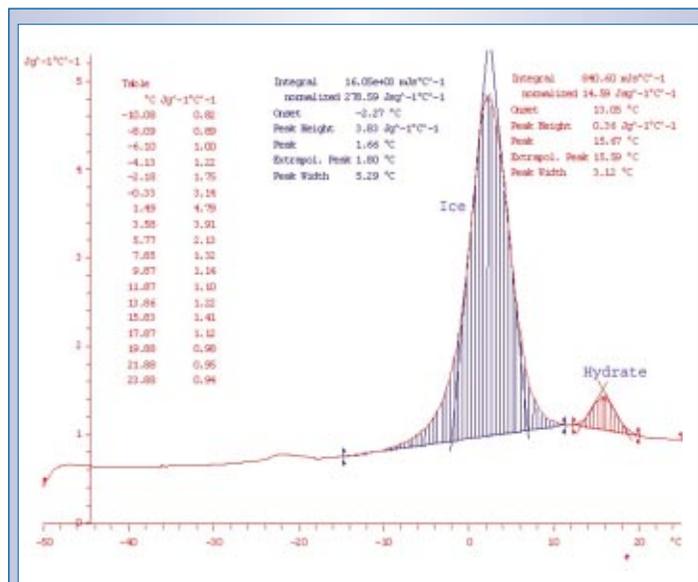


Figure 13: Heat capacity vs. temperature data of a DSC scan for a field sample from the Gulf of Mexico showing ice and hydrate.

onset by 44.6°F (7°C). The selected anti-agglomerant was also effective enough to suppress the hydrate crystallization by 53.6°F (12°C).

Hydrate nucleation and growth kinetics have been investigated through time temperature transformation (TTT) curves using the DSC, with and without 0.5% of PVP kinetic inhibitor. The experiments were performed by rapidly quenching the sample to the experimental temperature and the subsequent time until crystallization was measured. When performed over a range of temperatures, the results will give rise to the TTT curves as shown in Figure 12. The TTT curves separate the nucleation and growth kinetics. The minima or the “nose” of the TTT curve indicates the maximum growth rate. So the best performance of an inhibitor is measured on the basis of the amount of shift of the nose of the curve to longer times and lower temperature. Comparison of current crystallization data for the THF model system with and without the kinetic inhibitor shows good agreement with literature data (Koh et al., 2000) as shown in Figure 12. Figure 13 presents the most recent heat capacity

measurements completed for a field hydrate sample from the Gulf of Mexico supplied by the U.S. Naval Research Laboratory.

Field Testing and Future Plans

Field tests at the recently completed GTI/CEESI hydrate test loop at Nunn, Colo., will begin soon, with the measurements of gas hydrate formation and dissociation with and without low dosages of methanol, using the GTI laser imaging tool installed on the loop. GTI subcontract work for a DOE/CEESI project, Hydrate Control in Gas Storage Wells and Gathering Lines during Rapid Withdrawal Operations, has begun.

An addition of a T64000 Raman Spectrometer to GTI’s Hydrate Flow Assurance facility is in progress. The installation will be completed during the summer 2003. This will enable GTI to make real-time structural transition measurements in natural gas hydrates, from Structure II at low pressures to Structure I at high pressures, and to understand the plug dissociation kinetics. Test results are expected to help the gas industry predict

the plug dissociation time as a function of pressure and structure. ♦

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U.S. Department of Energy's National Energy Technology Laboratory. Details at www.gastechnology.org.

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